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Performance of RCRA (Resource Conservation and Recovery Act) Method 8280 for the Analysis of Dibenzo-P-Dioxins and Dibenzofurans in Hazardous Waste Samples

Lockheed Engineering and Management Services Co., Inc., Las Vegas, NV

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PERFORMANCE OF RCRA METHOD 8280 FOR THE ANALYSIS OF DIBENZO-P-DIOXINS AND DIBENZOFURANS IN HAZARDOUS WASTE SAMPLES

by

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16. ABSTRACT

Further evaluation of RCRA Method 8280 for the analysis of chlorinated dibenzo-p-dioxins and dibenzofurans has been performed. The Method has been modified to enable the quantitation of total tetra- through octa-chlorinated dioxins and dibenzofurans and has been applied to six different sample matrices derived from industrial polychlorophenol sources and also to fly-ash, still-bottom, and Missouri soil samples. An interlaboratory validation of the Method has been conducted in two phases: Phase I required the analysis of spiked and unspiked clay and sludge samples for certain specified analytes, and Phase II required the analysis of 10 samples of soil, sludge, fly-ash, and furans. Method detection limits of $^{13}C_{12}$-labeled polychlorinated dioxins and dibenzofurans in seven matrices have been determined. In order to propose the most effective procedure, a comparison was made of the Contract Laboratory Program carbon column cleanup (without backflush) with the backflush procedure used in the proposed RCRA Method.

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FOREWORD

On a molecular basis, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is one of the most poisonous synthetic chemicals known.[1] The compound has been shown in animals to possess teratogenic, embryotoxic, carcinogenic, and co-carcinogenic properties in addition to acute toxicity. Because of its chemical stability, lipophilic character, and extreme toxicity, it presents potentially severe health hazards to the human population. Although 2,3,7,8-TCDD is the most toxic of the 75 chlorinated dibenzo-p-dioxins (PCDD's), many of the others (and also of the 135 chlorinated dibenzofurans [PCDF's] which have similar genesis, structures, and properties) are known to possess relatively high toxicity to humans and animals. For this reason, the entire spectrum of PCDD's and PCDF's is of environmental concern. 2,3,7,8-TCDD was first synthesized in 1872,[2] and only sporadic reports of the preparation of PCDD's, containing two, four, or eight chlorine atoms, appeared in the years 1941-1965. Particular interest in 2,3,7,8-TCDD, and in the PCDD's and PCDF's in general, increased markedly with the discovery in the early 1970's of the same teratogenic and toxic effects with certain commonly used herbicides, e.g., 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), as were observed with 2,3,7,8-TCDD. Analysis of 116 samples of 11 different pesticides produced during the period 1950-1970 revealed the presence of PCDD contamination (tetra- through octachlorinated) in 42 percent of the samples.[3] Consideration of the chemistry of pesticide manufacture indicated that PCDD's could be formed in competing side-reactions of the polychlorophenol precursors. The domestic use of 2,4,5-T was subsequently banned, and the military use of Agent Orange (1:1 mixture of 2,4,5-T and 2,4-dichlorophenoxyacetic acid) as a defoliant in Vietnam was discontinued, both in the early 1970's. Because of the widespread usage of pesticides potentially contaminated with PCDD's, a Dioxin Monitoring Program was set up by the EPA in 1973 to develop an analytical method capable of detecting 2,3,7,8-TCDD in environmental samples at the part per trillion (ppt) level. This effort formed the basis of the National Dioxin Strategy of the Agency.

Although the most ubiquitous routes of non-occupational exposure of the general population to dioxins have probably been *via* the use of contaminated pesticides and from the emissions of municipal waste incinerators, the most concentrated waste sources of 2,3,7,8-TCDD are the tars and sludges resulting from the commercial preparation of 2,4,5-trichlorophenol (2,4,5-TCP). This latter fact was highlighted during an investigation in 1975-1977 of unexplained animal deaths at various horse arenas in Missouri.[4] It was discovered that the sites had been sprayed with a mixture of waste oil and distillation residues from the manufacture of 2,4,5-TCP which were contaminated with 2,3,7,8-TCDD. Subsequent investigation of chemical waste dump-sites in New York State (Hyde Park; Love Canal), where wastes from the manufacture of 2,4,5-TCP had been buried, also revealed the presence of substantial amounts of 2,3,7,8-TCDD.

Based on this experience, it was concluded by the EPA that samples containing tetra-, penta-, and hexa-CDD's and CDF's are likely to exhibit increased toxicity,[5] and a method to analyze hazardous wastes for the relevant PCDD's and PCDF's was included in the Resource Conservation and Recovery Act (RCRA) requirements for hazardous waste monitoring as published in the Federal Register.[6] A single-laboratory evaluation of the RCRA Method 8280 for the analysis of PCDD's and PCDF's in hazardous waste has been the subject of a previous report prepared for the Office of Solid Waste.[7] That report presented results obtained with sample matrices including pottery clay, a Missouri soil, a fly-ash, a still-bottom from a chlorophenol-based herbicide production process and an industrial process sludge. Major revisions to the Method as first published in 1983 were necessary to accommodate the analysis of complex samples such as sludge and still-bottom.

The revised Method 8280 has subsequently undergone a period of continual development, and this report presents results obtained during the further evolution of the Method. New documentation in this report includes Method performance data on complex samples from polychlorophenol use processes, results from an interlaboratory study of the revised Method, and method detection limits of selected PCDD's and PCDF's in a variety of matrices.

ABSTRACT

Further evaluation of RCRA Method 8280 for the analysis of chlorinated dibenzo-p-dioxins and dibenzofurans has been performed. The Method has been modified to enable the quantitation of total tetra- through octa-chlorinated dioxins and dibenzofurans and has been applied to six different sample matrices derived from industrial polychlorophenol sources and also to fly-ash, still-bottom, and Missouri soil samples. An interlaboratory validation of the Method has been conducted in two phases: Phase I required the analysis of spiked and unspiked clay and sludge samples for certain specified analytes, and Phase II required the analysis of 10 samples of soil, sludge, fly-ash, and still-bottom for total tetra- through octa-chlorinated dioxins and dibenzofurans. Method detection limits of $^{13}C_{12}$-labeled polychlorinated dioxins and dibenzofurans in seven matrices have been determined. In order to propose the most effective procedure, a comparison was made of the Contract Laboratory Program carbon column cleanup (without backflush) with the backflush procedure used in the proposed RCRA Method.

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ABBREVIATIONS

CLP	- Contract Laboratory Program
DFTPP	- decafluorotriphenylphosphine
EICP	- extracted ion current profile
GC	- gas chromatography
GC/MS	- gas chromatography/mass spectrometry
HpCDD	- heptachlorodibenzo-p-dioxin
HpCDF	- heptachlorodibenzofuran
HxCDD	- hexachlorodibenzo-p-dioxin
HxCDF	- hexachlorodibenzofuran
K-D	- Kuderna-Danish
MDL	- method detection limit
MID	- multiple ion detection
ND	- not detected
OCDD	- octachlorodibenzo-p-dioxin
OCDF	- octachlorodibenzofuran
PCDD	- polychlorinated dibenzo-p-dioxin
PCDE	- polychlorinated diphenyl ether
PCDF	- polychlorinated dibenzofuran
PCP	- pentachlorophenol
PeCDD	- pentachlorodibenzo-p-dioxin
PeCDF	- pentachlorodibenzofuran
ppb	- parts per billion
ppt	- parts per trillion
RCRA	- Resource Conservation and Recovery Act
RSD	- relative standard deviation
SD	- standard deviation
2,4,5-T	- 2,4,5-trichlorophenoxyacetic acid
TCDD	- tetrachlorodibenzo-p-dioxin
TCDF	- tetrachlorodibenzofuran
TCP	- trichlorophenol

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SECTION 1

INTRODUCTION

RCRA Method 8280 for the analysis of chlorinated dibenzo-p-dioxins and dibenzofurans, as published in the Federal Register in April 1983,[6] revealed the need for several modifications to allow for the determination of the target analytes in complex matrices, such as industrial sludge and still-bottom samples. Details of the modifications made and of the subsequent application of the revised Method to a limited number of samples analyzed in the course of a single-laboratory evaluation have been reported.[7]

Subsequently, the Method has been further refined in several important areas, as was needed to meet the needs of the characterization and assessment aspects of RCRA. A summary of these changes is as follows: In order to improve the accuracy of quantitation of the hepta- and octa-CDD's and CDF's, a second internal standard ($^{13}C_{12}$-OCDD) is added together with $^{13}C_{12}$-2,3,7,8-TCDD prior to sample workup. Some of the ions specified in the multiple ion detection (MID) descriptors have been changed so as to increase sensitivity by monitoring the most intense ion in the isotopic cluster. To ensure that co-eluting polychlorinated diphenyl ethers (PCDE's) are not contributing to the signal response due to PCDF's, the molecular ion of the appropriate PCDE was included in each MID descriptor. In addition, the criteria for the positive identification of PCDD and PCDF isomers were made more explicit. Instrument tune criteria employing perfluorotri-n-butylamine (FC-43) were substituted for those based on the use of decafluorotriphenylphosphine (DFTPP). The section on the calculation of concentrations of analytes was expanded to include a procedure for measuring unknown PCDD and PCDF isomers.

This report presents data on the performance of the Method as it was applied to the analysis of a variety of wastes derived from the use of polychlorophenols in the wood-preserving industry. As an additional test of Method performance, an interlaboratory validation study was conducted in two parts. A two-part study was used because the Method had been extensively revised since its publication in the Federal Register, and it was felt that participating laboratories would be unfamiliar with some of the proposed procedures. The first phase was intended to allow the participants to acquire familiarization with the Method by analyzing relatively simple matrices for a few specified analytes which had been spiked into the samples. The second phase required the total quantitation of tetra- through octa-CDD's and CDF's in complex samples containing the analytes at both low and extremely high levels; no spiking was used for these samples. A method detection limit study using all available $^{13}C_{12}$-labeled PCDD and PCDF isomers spiked into seven different sample matrices has also been performed. A comparison of the EPA Contract Laboratory Program (CLP) carbon column cleanup without and with a backflush elution procedure was

conducted to test the adequacy of the CLP method for the determination of total PCDD's and PCDF's.

SECTION 2

CONCLUSIONS

The single-laboratory application of the Method to the determination of PCDD's and PCDF's in complex environmental samples (e.g., fly-ash, still-bottom, and wastes from the industrial use of penta- and tri-chlorophenol) has routinely yielded high recoveries (60 to 85 percent) of the spiked internal standard, $^{13}C_{12}$-2,3,7,8-TCDD. This indicates that the extraction and cleanup procedures are able to accommodate samples ranging from those with a high aqueous content to viscous oils and chemical sludges. It can be assumed that endogenous PCDD's and PCDF's are extracted with equal success if matrix effects are not operating.

In the absence of a full range of standard reference materials, the accuracy of the Method is rather difficult to assess. However, data obtained from Phase I of the interlaboratory study indicate that the Method is biased high and that the bias appears to decrease as the concentrations of the analytes increase. Data from the method detection limit (MDL) study can be used as an indicator of intralaboratory precision. For seven replicate determinations of a TCDF and a PeCDD in fly-ash with each at a measured concentration of 2.6 times their final calculated MDL's, the relative standard deviations (RSD's) were 12.3 percent and 12.2 percent, respectively. Similar determinations for a PeCDF and a TCDD which were measured at a level 6.0 and 4.4 times their MDL's gave RSD's of 5.2 percent and 7.2 percent, respectively.

Encouraging results were obtained from Phase I of the interlaboratory study in which specific analytes spiked into clay and sludge samples were quantitated.

The good overall recovery (greater than 50 percent) of the internal standard and the small differences between the spiked concentrations and the mean measured values both indicate that the Method can provide acceptable data in a multi-laboratory program. Phase II of the interlaboratory study which required the quantitation of total tetra- through octa-CDD's and CDF's in 10 aliquots of 4 sample types also provided generally satisfactory results. The internal standards ($^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-OCDD) were recovered in overall acceptable yields ranging from 51 to 82 percent. However, quantitation of the analytes was less precise than in Phase I. Two major, probable reasons for this are as follows:

- the complex samples themselves, some of which contained endogenous amounts of the target analytes at low and at extremely high levels. This required a large dilution effect which minimized the value of the internal standard, and

- the analysis required the identification, confirmation, and quantitation of an unknown number of peaks for each congener often without an authentic reference material which could be used to confirm the identification.

Statistical analysis of the Phase II data revealed that:

- the recovery of the $^{13}C_{12}$-2,3,7,8-TCDD internal standard was a function of sample type whereas that of the $^{13}C_{12}$-OCDD internal standard was not;

- the laboratories were equivalent in accuracy for all analytes except OCDD; and

- the laboratories were equivalent in precision for 31 of the 40 possible matrix/analyte combinations.

The comparison of the Contract Laboratory Program (CLP) carbon column cleanup (backflush procedure is not used) with the backflush procedure used in Method 8280 indicated that although the CLP cleanup as written is very satisfactory for the determination of 2,3,7,8-TCDD (and possibly other tetra- and penta-CDD's and CDF's), it is not adequate for the determination of hexa-, hepta-, and octa-CDD's and CDF's. However, the combination of open carbon column with a backflush procedure gave acceptable performance for the tetra- through octa-substituted congeners.

Method detection limits of eight $^{13}C_{12}$-labeled PCDD's and PCDF's spiked into reagent water were found to be in the low ppt range (less than 10 ppt); 42 of 48 values determined for 6 environmental samples were less than 5 ppb.

SECTION 3

RECOMMENDATIONS

As a result of the experience gained during the single- and multi-laboratory testing of the Method with a variety of environmental samples, several modifications to the Method and areas of further study are recommended:

1. The Method should allow for the use of disposable, open carbon columns as an option to the currently specified HPLC carbon column cleanup. This would allow for an increase in the rate of sample throughput and would also reduce solvent consumption.

2. The use of stacked acidic/basic silica gel columns instead of multiple liquid-liquid partitioning in the extraction/cleanup procedures should be investigated. This would eliminate the problems of emulsion formation currently encountered and would also greatly reduce the quantities of corrosive wastes generated.

3. Gas chromatography (GC) conditions should be modified to improve the resolution between the internal standard ($^{13}C_{12}$-2,3,7,8-TCDD) and the recovery standard ($^{13}C_{12}$-1,2,3,4-TCDD). If this cannot be readily achieved, then use of an alternative recovery standard should be considered.

4. The elution windows (defined by first and last eluting isomers) of the tetra- through octa-CDD and CDF congeners should be established for the GC conditions used in the Method.

5. Because of the known elution overlap of some tetra-substituted isomers with penta-substituted isomers (and other potential overlaps between homologous groups), the multiple ion detection (MID) descriptors should be modified to include at least one ion for each overlapping homologue.

6. Method 8280 should be written to require as many GC/MS analyses as necessary by using the appropriate MID descriptors whenever an elution overlap is noted in a sample.

7. Kovats Indices should be determined for available PCDD's and PCDF's. This would aid laboratories in the identification of isomers not known or available to them and would be useful in a GC screening program.

8. The need to monitor for polychlorinated diphenyl ethers (PCDE's) in the final sample extract should be investigated.

9. A source of a well-defined GC performance standard should be identified. Column performance guidelines should be established for a variety of columns.

10. Sample reanalysis requirements given the presence of low and of very high levels of target analytes should be defined.

SECTION 4

COMPARISON OF CLP CARBON COLUMN CLEANUP WITH BACKFLUSH PROCEDURE ADAPTED FROM RCRA METHOD 8280

The major difference between the Contract Laboratory Program (CLP) Low Resolution Dioxin Method and RCRA Method 8280 is one of objective. For the CLP Method, it is the determination of 2,3,7,8-TCDD only whereas for RCRA Method 8280 it is the determination of total concentrations of all tetra- through octa-chlorinated dibenzo-p-dioxins and dibenzofurans. This has led to technical differences during the development of the Methods, and a side-by-side comparison of the carbon column cleanup employed by the two Methods is shown in Table 4-1. It can be seen that, once the column has been prepared, the CLP method should be faster and consume much less solvent. In addition, the CLP method does not require HPLC equipment. It was therefore of interest to determine whether the CLP carbon column cleanup, as written, was adequate for analysis for PCDD's and PCDF's.

The major operating difference between the two carbon column cleanup methods is the use of a toluene backflush in Method 8280 to elute the analytes of interest. To evaluate the applicability of the CLP procedure for the analysis of higher PCDD's and PCDF's, a gravity-feed carbon column using a cut-down disposable serological pipet (20 cm x 6 mm i.d.) was prepared and was pre-eluted as directed. The column was spiked with 25 µL of a standard solution containing 11 PCDD's and PCDF's each at 10 ng/µL and was eluted using the specified eluents. After collection of the toluene fraction (2 mL) which was held separately, the column was eluted with an additional 5 mL of toluene. The toluene fractions were concentrated separately to 500 µL, and each was analyzed by GC/ECD; the analytes were quantitated against an internal standard, endrin ketone. A second column was prepared, spiked, and eluted as described above except that it was reversed before collection of the two toluene fractions (2 mL and 5 mL).

The percentage recovery of each PCDD and PCDF in each fraction for the column elution with and without the backflush procedure is shown in Table 4-2. The data reveal that, for the particular isomers used, the CLP method as written without backflush procedure gives acceptable recoveries only for the tetra- and penta-CDD's and CDF's. Recovery of the hexa- and hepta-CDD's and CDF's is low while the OCDD and OCDF are not recovered at all. The additional 5 mL toluene fraction elutes significant amounts of the higher substituted congeners although the total recovery of the OCDD and OCDF still remains low. Results obtained using the backflush procedure show that the 2 mL toluene fraction eluted very much greater amounts of the hexa-, hepta-, and octa-isomers than did the procedure without the backflush. The total recovery for

TABLE 4-1. COMPARISON OF CARBON COLUMN CLEANUP METHODS

CLP Method	Method 8280
1. Column Preparation: Mix 3.6 g Carbopack C with 16.4 g of Celite 545 in a 40 mL vial and activate by heating at 130°C for 6 hours. Check each new batch to ensure TCDD recovery $\geq$ 50 percent; use the low level concentration standard. Insert a glass wool plug in a 15 cm by 7 mm O.D. disposable pipet. Apply suction to the pointed end of the pipet and add the prepared mixture to form a 2 cm column.	1. Column Preparation: A 10 mm x 7 cm silanized glass HPLC column is prepared by mixing 5 percent (w/w) AX-21 active carbon with 10 µm silica (Spherisorb S10W). Stir and sieve through a 40 µm screen.
2. Pre-elute the column with: 2 mL toluene 1 mL 75/20/5 (v/v) methylene chloride/methanol/benzene 1 mL 50/50 (v/v) cyclohexane/methylene chloride 2 mL hexane	2. Evaporate the 60 percent methylene chloride/hexane fraction to 400 µL and prepare for transfer to a 1 mL HPLC loop injector. Rinse the tube with 500 µL hexane and add both fractions to the HPLC injector loop.
3. While the column is still wet with hexane, add the sample extract and elute with the following sequence: 2 mL hexane 1 mL 50/50 (v/v) cyclohexane/methylene chloride 1 mL 75/20/5 (v/v) methylene chloride/methanol/benzene Discard the eluates. Elute with 2 mL toluene and collect the eluent, store until GC/MS analysis.	3. Elute the column with 30 mL cyclohexane/methylene chloride 1:1 (v/v) at 2 mL/min. Discard the effluent. Next elute with 10 mL 70/20/5 (v/v) methylene chloride/methanol/benzene. Discard the effluent. Backflush the column with 40 mL toluene collecting the effluent which contains the PCDD's and PCDF's. Clean the column with 30 mL methanol followed by 40 mL toluene in the backflush position. Return to normal position and equilibrate by pumping through 30 mL 1:1 (v/v) cyclohexane/methylene chloride. Check for bleed after high level (>500 ppb) samples and replace as needed.
	4. Evaporate the toluene fraction on a rotary evaporator at 50°C. Transfer to a 2.0 mL reactivial using a toluene rinse and concentrate to the desired volume using nitrogen.

TABLE 4-2. PERCENT RECOVERY[a] OF PCDD'S AND PCDF'S FROM CLP CARBON COLUMN

Analyte	Method as Written (without Backflush)			Method Modified (with Backflush)		
	2 mL Toluene Fraction	Additional 5 mL Toluene Fraction	Total	2 mL Toluene Fraction	Additional 5 mL Toluene Fraction	Total
2,3,7,8-TCDF	81.5	ND	81.5	83.0	ND	83.0
1,2,3,4-TCDD	80.0	ND	80.0	80.3	ND	80.3
2,3,7,8-TCDD	87.6	ND	87.6	87.6	ND	87.6
1,2,3,7,8-PeCDF	71.0	14.0	85.0	85.4	ND	85.4
1,2,3,4,7-PeCDD	80.9	ND	80.9	87.5	ND	87.5
1,2,3,4,7,8-HxCDF	35.9	43.0	78.9	74.5	9.8	84.3
1,2,3,4,7,8-HxCDD	39.6	46.0	85.6	80.3	9.8	90.1
1,2,3,4,6,7,8-HpCDF	7.8	52.6	60.4	54.4	25.5	79.9
1,2,3,4,6,7,8-HpCDD	13.4	62.0	75.4	57.8	22.6	80.4
1,2,3,4,6,7,8,9-OCDD	ND	50.8	50.8	48.2	25.8	74.0
1,2,3,4,6,7,8,9-OCDF	ND	36.0	36.0	45.7	26.9	72.6

[a]Results of a single determination.
ND = Not detected.

each isomer was also equal to or greater than that obtained without the backflush procedure. It is evident that while the CLP carbon column cleanup is satisfactory for analysis for 2,3,7,8-TCDD (and possibly other tetra- and penta-CDD's and CDF's), it is not adequate for the determination of hexa-, hepta-, and octa-CDD's and CDF's. However, use of an open column technique which does not require liquid chromatography equipment should improve the rate of sample throughput by enabling many samples to be processed concurrently. For this reason and because of the acceptable recoveries demonstrated using a backflush procedure with the gravity-feed carbon column, it is recommended that the open column cleanup described below should be included as an option to the HPLC carbon column cleanup specified in Method 8280.

OPEN CARBON COLUMN CLEANUP

Prepare a standard 5-mL disposable pipet by cutting off 1 cm from the tip. Insert a glasswool plug at the 2.5 mL mark and pack with 300 mg of charcoal/silica gel. Cap the packing with a glasswool plug. Prerinse the column with 5 mL hexane in the forward direction of flow and then in the reverse direction of flow. While still in the reverse direction of flow, pre-elute the column with 2 mL of toluene, 1 mL of methylene chloride/methanol/benzene (75:20:5, v/v), 1 mL of cyclohexane/methylene chloride (50:50, v/v), and 2 mL of hexane. Discard all column rinsates. Still in the reverse direction of flow, transfer the sample concentrate to the column and elute with 1 mL of hexane, 1 mL of hexane, 1 mL of cyclohexane/methylene chloride (50:50, v/v), and 1 mL of methylene chloride/methanol/benzene (75:20:5, v/v). Discard all of the above eluates. Now turn the column over and in the direction of forward flow elute PCDD's and PCDF's with 15 mL of toluene. Proceed with the next step of the analysis using this toluene fraction.

NOTE: The charcoal/silica gel packing is prepared by thoroughly mixing Carbopack C (3.6g) and silica gel (16.4g) followed by activation at 130°C. for 6h.

SECTION 5

ANALYSIS OF WASTES FROM INDUSTRIAL USE OF CHLOROPHENOLS

Eleven waste samples derived from the industrial use of pentachlorophenol (PCP) and 10 samples derived from the industrial use of trichlorophenol (TCP) were provided by the EPA. The 21 samples together represent 6 different matrix types, viz. sludge, fuel oil, alcohol fuel oil, soil, water, and sawdust. The range of matrix types encompassed is expected to be representative of those to be analyzed under RCRA regulations and is expected to provide varying degrees of sample complexity.

Each sample was analyzed in duplicate for the quantitation of total tetra- through octa-CDD's and CDF's. Two criteria were applied to confirm that peaks in the extracted ion current profiles (EICP's) of the quantitation ions were due to the targeted analytes and were not due to either interferences or spurious noise signals. These were the following:

- signal-to-noise ratio greater than 3 to 1
- the presence of the confirmation ion (listed in Table 3 of the Method) such that the relative intensity of the quantitation ion and the confirmation ion was within the limits specified in the Method, Table 4 (see Appendix B).

Signal responses that did not meet these criteria are reported as "ND" (not detected). Quantitation was usually performed against $^{13}C_{12}$-2,3,7,8-TCDD as the internal standard, and values are corrected for the recovery using this compound as an isotopic diluent. However, due to the extremely high levels of hexa-, hepta-, or octa-CDD's/CDF's present in some samples, these analytes were quantitated against $^{13}C_{12}$-1,2,3,4-TCDD or $^{13}C_{12}$-OCDD added to the extracts after dilution. It is a disadvantage of the quantitation method that multiple GC/MS analyses are therefore required for samples containing both low and high level analytes. To spike the sample with the appropriate ^{13}C-standard would have caused an unnecessarily large expense. Whenever possible, sample re-run requirements should be imposed to lessen the used for quantitation by anything other than the isotopic diluent. Several characteristics are evident in the data presented in Tables 5-1 and 5-2. First is the total absence of detectable levels of TCDD in all of the 21 samples and the occurrence of PeCDD in only 3 samples. Second are the very high levels of hepta- and octa-CDD present in 10 of 11 PCP process samples; the presence of only very low levels of analytes in the remaining PCP process sample (B-5) was not unexpected in view of the known low solubility of PCDD's/PCDF's in water. The proposed detection limit achieved for wastewater (0.01 ppb) is a reflection both of the absence of interferences in the sample and of the subsequent facile extraction and cleanup

TABLE 5-1. ANALYSIS[a] OF PCP PROCESS SAMPLES USING METHOD 8280

PCDD/ PCDF	Sludge B-6d (ppb)	Fuel oil B-7b (ppb)	Sludge B-8b (ppb)	Sludge B-12h (ppb)	Fuel oil A-2g (ppb)	Alcohol fuel oil A-3g (ppb)	Sludge A-4g (ppb)	Soil A-5g (ppb)	Soil A-6.1g (ppb)	Soil A-6.2g (ppb)
TCDD	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND
PeCDD	ND	ND	ND	ND	ND	ND	ND	ND	27	ND
HxCDD	2150	2186	ND	ND	2079	762	726	283	730	396
HpCDD	51520[c]	67176[c]	2166[c]	978[c]	38195[c]	17956[c]	59600[c]	12945[c]	24700[c]	12300[c]
OCDD	72300[c]	154000[c]	2670[c]	2550[c]	59100[c]	24500[c]	106000[c]	15500[c]	26300[c]	15000[c]
TCDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PeCDF	ND	154	ND	ND	246	ND	ND	ND	61	ND
HxCDF	68	2933	ND	ND	2852	76	1568	65	252	56
HpCDF	343	1342	ND	ND	1913	1118	1948	533	1695	434
OCDF	4100[c]	7500[c]	ND	76	447	741	3200[c]	900[c]	3080[c]	1690[c]
$^{13}C_{12}$-2,3,7,8-TCDD percent recovery	66.8	69.0	64.3	67.8	69.2	60.0	62.9	77.0	75.4	74.8

[a]Mean of duplicates; concentrations shown are for the total of all isomers within a given homologous series.

[b]ND is below the detection limit for the sample matrix. Detection limits are estimated as 5 ppb for the tetra- through hexa-isomers, and 10 ppb for the hepta- and octa-isomers.

[c]Due to the extremely high levels of HpCDD, OCDD, and OCDF detected in the GC/MS analysis, the extracts were diluted after normal quantitation of the tetra-, penta-, hexa-CDD/CDF and hepta-CDF. HpCDD, OCDD, and OCDF were then quantitated versus $^{13}C_{12}$-1,2,3,4-TCDD added after dilution; the values are corrected for $^{13}C_{12}$-2,3,7,8-TCDD recovery.

TABLE 5-2. ANALYSIS[a] OF PCP PROCESS SAMPLE (B-5) AND 10 TCP PROCESS SAMPLES USING METHOD 8280

PCDD/ PCDF	Water B-5 (ppb)	Sawdust H-3 (ppb)	Soil H-7a (ppb)	Soil H-7b (ppb)	Soil H-7c (ppb)	Water I-1 (ppb)	Sludge I-2 (ppb)	Sludge I-11 (ppb)	Soil I-12c (ppb)	Soil I-14a (ppb)	Soil I-14b (ppb)
TCDD	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PeCDD	ND	385	ND	ND	ND	ND	30	ND	ND	ND	ND
HxCDD	0.072	2680[d]	ND	ND	ND	110[d]	2410[d]	399	ND	ND	ND
HpCDD	2.5[c]	2314[c]	ND	ND	ND	1677[c]	42134[c]	4404[c]	ND	37	ND
OCDD	1.25[c]	1250[c]	5.5	ND	ND	345[c]	14658[c]	4080[c]	ND	20	ND
TCDF	0.024	3598[d]	ND	ND	ND	3.9[d]	201	68	ND	ND	ND
PeCDF	ND	1908[d]	ND	ND	ND	ND	429	23	ND	ND	ND
HxCDF	0.017	11903[d]	ND	ND	ND	233[d]	5496[d]	626	ND	ND	ND
HpCDF	0.136	1374[d]	ND	ND	ND	108[c]	2768[c]	622[c]	ND	ND	ND
OCDF	0.029	94[c]	ND	ND	ND	16[c]	239[c]	151[c]	ND	ND	ND
$^{13}C_{12}$-2,3,7,8-TCDD percent recovery	67.3	95.2[e]	71.2	76.4	72.3	---[f]	77.1	75.6	84.9	78.7	84.1

[a]Mean of duplicates, except for samples B-5 and I-1 which are the result of single determinations. Concentrations shown are for the total of all isomers within a given homologous series.

[b]ND is below the detection limit for the sample matrix. Detection limits are 5 ppb for soil, sawdust, sludge, and 0.01 ppb for water.

[c,d]Due to very high levels of some hexa-, hepta-, or octa-CCD/CDF isomers, some samples were diluted and the PCDD's and PCDF's noted were quantified versus $^{13}C_{12}$-OCDD[c] or $^{13}C_{12}$-1,2,3,4-TCDD[d]; the values are corrected for $^{13}C_{12}$-2,3,7,8-TCDD recovery.

[e]Some interference at the quantitation ion was noted.

[f]Gross interference at the quantitation ion was noted.

procedures. That the extraction and cleanup procedures work well for the matrix types examined is demonstrated by the generally high recovery (60 to 85 percent) of the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD. Interference at the quantitation ion of the internal standard was noted for only two samples (H-3, sawdust; I-1, water) which were both TCP process samples.

NOTES ON PHYSICAL CHARACTERISTICS AND EXTRACTION/CLEANUP OF SAMPLES

Sample B-5 — Clear, aqueous sample (wastewater from cooling tower). A yellow aqueous phase resulted from the base wash. A red-brown aqueous phase resulted from the first acid wash, and a colorless phase resulted from the second acid wash. No problems were encountered with emulsions.

Sample H-3 — Sawdust (spray-booth filter debris). The base wash gave a yellow aqueous layer. The first acid wash gave a dark brown aqueous layer, and the second acid wash gave a colorless layer. The emulsion required 15 to 20 minutes to clear after the first acid wash.

Sample H-7a — Soil (soil core from treated-wood storage yard). The acid wash was performed before the base wash. Three acid washes were required to progress from a dark brown to a colorless aqueous layer. The base wash gave a cloudy aqueous layer, but no emulsion. The subsequent water wash gave a bad emulsion which required ca. 15 minutes to clear.

Sample H-7b — Soil (saturated soil core with some water on top). Three acid washes were required to progress from a dark brown to a colorless aqueous layer. No problems were encountered with emulsions.

Sample H-7c — Soil (soil core sample was very wet mud, saturated with water). Two acid washes were required to progress from a dark yellow to a colorless aqueous layer. No emulsion problems were encountered.

Sample I-1 — Red, oily-looking water (aqueous dip tank solution). Performed four extractions with methylene chloride because of very bad emulsion formation.

A small amount of red sediment was observed in the K-D concentrate after performing the solvent exchange into hexane. The normal order of base/acid washes was therefore reversed. Two acid washes were required to progress from a dark brown to a colorless aqueous layer which was cloudy.

The base wash resulted in yellow scum on the aqueous layer. No emulsion problems were encountered.

Concentration of the organic extract after the acid/base wash sequence and again after the alumina column cleanup gave a

dirty film on the sides of the glass container. This film could not be re-dissolved in hexane but was washed onto the carbon column by methylene chloride/hexane (60:40 v/v).

Sample I-2 — Oily sawdust (dip tank sludge).

Two acid washes were required to progress from a yellow-orange to a colorless aqueous layer. No problems were encountered with emulsions.

Sample I-11 — Saturated sludge with 50 percent standing water (from catch basin sump). The extract was extremely dirty after K-D concentration. The normal order of base/acid washes was therefore reversed. Four acid washes were required to progress from a black to a yellow aqueous layer.

The water wash immediately following the post-acid wash gave a large amount of emulsion. The base wash gave an emulsion which immediately cleared.

Sample I-12c — Very wet soil (core from treated-wood storage yard).

One acid wash only was required.

No problems were encountered with emulsions.

Sample I-14a — Wet clay (soil core from treated-wood storage yard).

One acid wash only was required.

No problems were encountered with emulsions.

Sample I-14b — Wet lumpy clay (soil core from treated-wood storage yard).

On shaking with petroleum ether/methanol, the sample dispersed readily but did not appear to "turn over" well.

One acid wash only was required.

No problems were encountered with emulsions.

Some residue adhered to sides of the conical concentrator tube immediately prior to loading the carbon column.

Sample B-6d — Sludge (very thick - difficult to obtain a homogeneous sample). The toluene solution from the Dean-Stark separator contained a large amount of finely divided solid; filtration through Whatman No. 54 paper was very slow. The acid wash procedure gave a yellow aqueous phase even after four washes.

Sample B-7b — Sludge (high oil content).

	The aqueous layer was still very yellow after four acid washes.
Samples B-8b and B-12h	Sludge (high water content). The samples were cleaned-up readily due to low oil content. Only three acid washes were required to obtain a colorless aqueous phase.
Sample A-2g	Oil (no water content). The drying procedure using the Dean-Stark separator was omitted because of the absence of water. The aqueous layer was still yellow after three acid washes.
Sample A-3g	Alcohol fuel oil. The sample was very viscous; the toluene extract filtered very slowly. A large amount of emulsion formed during the first acid wash.
Sample A-4g	Sludge (high oil content). The drying procedure using the Dean-Stark separator was omitted because of the absence of water. The acid wash was performed before the base wash.
Sample A-5g	Soil (contained some oil). The base wash gave a strong yellow aqueous layer.
Samples A-6.1g and A-6.2g	Soil. A finely divided solid adhered to the K-D apparatus after concentration of the hexane solution.

SECTION 6

METHOD DETECTION LIMIT STUDY

For purposes of this study, the method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a given matrix containing the target analyte. The experimental design for this study (Appendix A) was that reported by Glaser et al.,[8] and was applied using all available $^{13}C_{12}$-labeled analytes spiked into seven different sample types at a concentration of twice the estimated MDL of each analyte. This experimental design was used in order to obtain MDL values in each matrix of interest without spiking the matrix with unlabeled PCDD's and PCDF's and without changing the integrity of the matrix. In order to establish an appropriate spiking level, the MDL was estimated as that concentration at which the response of the appropriate quantitation ion gave a signal/noise ratio of 3 to 1. Statistical considerations required that a minimum of seven replicates of each sample type should be processed through the entire analytical method. Two initial replicates were tested to verify the reasonableness of the MDL estimate for each sample type. When a reasonable spiking level had been achieved, five more determinations were made at the same spiked concentration. The standard deviation (S) of the mean concentration determined for each analyte was calculated from the seven replicate measurements for each of the seven matrix types. The MDL was then calculated from the equation:

$$MDL = t_{(n-1,\ 1-\alpha\ =\ 0.99)} \times (S)$$

where $t_{(n-1,\ 1-\alpha\ =\ 0.99)}$ is the Student's t value appropriate for a 99 percent confidence level and a standard deviation estimate with n-1 degrees of freedom.

Therefore,

$$MDL = 3.143(S).$$

The concentration (C_S) of each analyte in each sample was determined with reference to the $^{13}C_{12}$-1,2,3,4-TCDD internal standard, which was spiked after sample workup to give a final concentration of 40 pg/μL, using the following equation:

$$C_S = \frac{A_S \times C_{IS}}{A_{IS} \times RF}$$

where

A_S = response (area) of analyte

A_{IS} = response (area) of $^{13}C_{12}$-1,2,3,4-TCDD

C_{IS} = concentration of $^{13}C_{12}$-1,2,3,4-TCDD (40 pg/μL)

RF = response factor of the analyte.

The response factor (RF) used for each analyte was the mean of five determinations calculated from a linear, 5-point calibration curve (constructed by the use of standards) according to the equation:

$$RF = \frac{A_S \times C_{IS}}{A_{IS} \times C_S} .$$

The use of $^{13}C_{12}$-1,2,3,4-TCDD as an internal standard rather than $^{13}C_{12}$-2,3,7,8-TCDD allowed the determination of the MDL of the latter analyte. The samples included in this study were selected to provide a representative range of matrices of environmental interest, and they are described below.

Reagent water: distilled, deionized laboratory water.

Missouri soil: soil blended to form a homogeneous sample.

Fly-ash: alkaline ash recovered from the electrostatic precipitator of a coal-burning power plant.

Industrial sludge: sludge from cooling tower which received creosotic and pentachlorophenolic wastewaters. Sample was ca. 70 percent water mixed with oil and sludge.

Still-bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.

Fuel oil: wood-preservative solution from the modified Thermal Process tanks. Sample was an oily liquid (>90 percent oil) containing no water.

Fuel oil/Sawdust: sawdust was obtained as a very fine powder from the local lumber yard. Fuel oil (described above) was mixed at the 4 percent (w/w) level.

The eight $^{13}C_{12}$-labeled PCDD's and PCDF's used in this study and their MDL's in the seven sample matrices are listed in Table 6-1. Several characteristics and trends are apparent in the data: $^{13}C_{12}$-2,3,7,8-TCDD/TCDF usually had the lowest MDL values for each sample type while $^{13}C_{12}$-HpCDD/OCDD usually had the highest; as might be expected, the MDL values for all analytes generally increased in passing from the "clean" sample types (reagent water, fly-ash) to the more complex, organics-containing matrices (still-bottom, industrial

TABLE 6-1. METHOD DETECTION LIMITS OF $^{13}C_{12}$-LABELED PCDD'S AND PCDF'S IN REAGENT WATER (PPT) AND ENVIRONMENTAL SAMPLES (PPB)

$^{13}C_{12}$-Labeled Analyte	Reagent Water[a]	Missouri Soil[b]	Fly-Ash[b]	Industrial Sludge[c]	Still-Bottom[d]	Fuel Oil[d]	Fuel Oil/ Sawdust[b]
2,3,7,8-TCDD	0.44	0.13	0.07	0.40	1.81	0.75	0.13
1,2,3,7,8-PeCDD	2.35	0.70	0.25	1.47	2.46	2.09	0.18
1,2,3,6,7,8-HxCDD	6.63	1.24	0.55	2.26	16.2	5.02	0.25
1,2,3,4,6,7,8-HpCDD	5.45	1.60	1.41	3.39	4.59	8.14	0.49
OCDD	7.37	1.35	2.27	7.68	10.1	23.2	1.34
2,3,7,8-TCDF	0.58	0.11	0.06	0.36	2.26	0.48	0.04
1,2,3,7,8-PeCDF	1.50	0.33	0.06	0.58	1.61	0.80	0.09
1,2,3,4,7,8-HxCDF	2.53	0.83	0.30	1.15	2.27	2.09	0.17

[a]Sample size 1,000 mL
[b]Sample size 10 g
[c]Sample size 2 g
[d]Sample size 1 g
Note: The final sample-extract volume was 100 µL for all samples.

sludge). The MDL for $^{13}C_{12}$-2,3,7,8-TCDD in reagent water (0.44 ppt) determined in this study using Method 8280 compares well with the value reported[8] for 2,3,7,8-TCDD in reagent water (2 ppt) which was determined using Method 613 (capillary column GC/MS with selected ion monitoring). The MDL procedure, involving seven replicate determinations of each of the eight analytes in each of seven sample matrices, also generated other data (percent recovery, precision) of interest in assessing the performance of Method 8280. These data are presented in Tables 6-2 through 6-8. It can be seen that good recoveries were obtained and that the precision at such low spike levels was acceptable.

TABLE 6-2. PERCENT RECOVERY OF $^{13}C_{12}$-LABELED PCDD'S AND PCDF'S FROM REAGENT WATER

$^{13}C_{12}$-Labeled Analyte	Concentration (pg/µL) in Final Extract		RSD Percent	Mean Recovery Percent
	Spiked	Measured		
2,3,7,8-TCDD	20	23.2	6.0	116.0
1,2,3,7,8-PeCDD	40	45.8	16.4	114.5
1,2,3,6,7,8-HxCDD	60	52.7	40.0	87.8
1,2,3,4,6,7,8-HpCDD	80	77.8	22.3	97.3
OCDD	100	91.3	25.7	91.3
2,3,7,8-TCDF	10	7.70	24.0	77.0
1,2,3,7,8-PeCDF	20	18.8	25.4	94.0
1,2,3,4,7,8-HxCDF	40	32.4	24.8	81.0

TABLE 6-3. PERCENT RECOVERY OF $^{13}C_{12}$-LABELED PCDD'S AND PCDF'S FROM MISSOURI SOIL

$^{13}C_{12}$-Labeled Analyte	Concentration (pg/µL) in Final Extract		RSD Percent	Mean Recovery Percent
	Spiked	Measured		
2,3,7,8-TCDD	40	37.3	11.0	93.3
1,2,3,7,8-PeCDD	80	65.3	33.9	81.6
1,2,3,6,7,8-HxCDD	120	72.1	54.9	60.1
1,2,3,4,6,7,8-HpCDD	160	88.2	57.8	55.1
OCDD	200	84.7	50.5	42.4
2,3,7,8-TCDF	20	15.7	22.5	78.5
1,2,3,7,8-PeCDF	40	34.3	30.1	85.8
1,2,3,4,7,8-HxCDF	80	58.8	44.9	73.5

TABLE 6-4. PERCENT RECOVERY OF $^{13}C_{12}$-LABELED PCDD'S AND PCDF'S FROM FLY ASH

$^{13}C_{12}$-Labeled Analyte	Concentration (pg/µL) in Final Extract		RSD Percent	Mean Recovery Percent
	Spiked	Measured		
2,3,7,8-TCDD	40	31.0	7.2	77.5
1,2,3,7,8-PeCDD	80	64.9	12.2	81.1
1,2,3,6,7,8-HxCDD	120	100.5	17.4	83.8
1,2,3,4,6,7,8-HpCDD	150	169.1	26.5	112.7
OCDD	250	235.8	30.6	94.3
2,3,7,8-TCDF	20	14.2	12.3	71.0
1,2,3,7,8-PeCDF	40	33.2	5.2	83.0
1,2,3,4,7,8-HxCDF	80	57.8	16.3	72.3

TABLE 6-5. PERCENT RECOVERY OF $^{13}C_{12}$-LABELED PCDD'S AND PCDF'S FROM INDUSTRIAL SLUDGE

$^{13}C_{12}$-Labeled Analyte	Concentration (pg/µL) in Final Extract		RSD Percent	Mean Recovery Percent
	Spiked	Measured		
2,3,7,8-TCDD	40	25.3	10.2	63.3
1,2,3,7,8-PeCDD	80	56.7	16.5	70.9
1,2,3,6,7,8-HxCDD	80	90.6	15.8	113.3
1,2,3,4,6,7,8-HpCDD	120	128.6	16.7	107.2
OCDD[a]	175	302.5	16.2	172.9
1,2,3,7,8-TCDF	20	15.6	14.6	78.0
1,2,3,7,8-PeCDF	40	26.4	14.1	66.0
1,2,3,4,7,8-HxCDF	80	49.5	14.8	61.9

[a]Peak shape was distorted by very high level of interferent.

TABLE 6-6. PERCENT RECOVERY OF $^{13}C_{12}$-LABELED PCDD'S AND PCDF'S FROM STILL-BOTTOM

$^{13}C_{12}$-Labeled Analyte	Concentration (pg/µL) in Final Extract		RSD Percent	Mean Recovery Percent
	Spiked	Measured		
2,3,7,8-TCDD[a]	40	57.3	10.1	143.3
1,2,3,7,8-PeCDD	80	58.1	13.5	72.6
1,2,3,6,7,8-HxCDD[a]	80	109.0	47.2	136.3
1,2,3,4,6,7,8-HpCDD	120	97.7	15.0	81.4
OCDD	175	197.6	16.3	112.9
2,3,7,8-TCDF[b]	20	14.5	49.7	72.5
1,2,3,7,8-PeCDF	40	24.5	20.9	61.3
1,2,3,4,7,8-HxCDF	80	64.8	11.2	81.0

[a]Low level interferent was observed; peak shape was not distorted.
[b]Peak shape was distorted by very high level of interferent.

TABLE 6-7. PERCENT RECOVERY OF $^{13}C_{12}$-LABELED PCDD'S AND PCDF'S FROM FUEL-OIL

$^{13}C_{12}$-Labeled Analyte	Concentration (pg/µL) in Final Extract		RSD Percent	Mean Recovery Percent
	Spiked	Measured		
2,3,7,8-TCDD	40	29.7	8.0	74.3
1,2,3,7,8-PeCDD	80	56.8	11.7	71.0
1,2,3,6,7,8-HxCDD	120	110.7	14.4	92.3
1,2,3,4,6,7,8-HpCDD	150	118.3	21.9	78.9
OCDD	250	232.8	31.7	93.1
2,3,7,8-TCDF	20	12.9	11.9	64.5
1,2,3,7,8-PeCDF	40	27.7	9.2	69.3
1,2,3,4,7,8-HxCDF	80	57.2	11.7	71.5

TABLE 6-8. PERCENT RECOVERY OF $^{13}C_{12}$-LABELED PCDD'S AND PCDF'S FROM FUEL OIL/SAWDUST

$^{13}C_{12}$-Labeled Analyte	Concentration (pg/µL) in Final Extract		RSD Percent	Mean Recovery Percent
	Spiked	Measured		
2,3,7,8-TCDD	40	32.4	12.7	81.0
1,2,3,7,8-PeCDD	80	57.0	10.1	71.3
1,2,3,6,7,8-HxCDD	120	92.2	8.5	76.8
1,2,3,4,6,7,8-HpCDD	150	120.6	12.8	80.4
OCDD	250	241.6	17.6	96.6
2,3,7,8-TCDF	20	13.1	10.6	65.5
1,2,3,7,8-PeCDF	40	28.0	10.4	70.0
1,2,3,4,7,8-HxCDF	80	52.7	10.4	65.9

SECTION 7

INTERLABORATORY TEST OF RCRA METHOD 8280

PHASE I

Phase I was intended to allow participating laboratories to acquire familiarization with the requirements of the revised RCRA Method 8280. A familiarization phase of the study was considered necessary since extensive revisions had been made to the original Method 8280. These included (1) changes in the procedure for the extraction of analytes from the sample, (2) modification of the open column alumina chromatography cleanup, (3) deletion of the HPLC cleanup, (4) addition of a carbon column cleanup, and (5) incorporation of internal and recovery standards into the Method.

Five laboratories were selected by the Contract Laboratory Program to participate in the study and were each provided with samples, analytical standards, isotopically labeled internal and recovery standards, and the revised Method. Detailed supplemental instructions which included guidance on the sample size, the volume of the final extract, typical MID descriptors, typical MID and RIC chromatograms, and the reporting of data and deliverables, were also provided. Each laboratory was provided with the following six samples which had been prepared by personnel of Lockheed-EMSCO who also analyzed a set of the six samples.

SAMPLE	TYPE
Clay Blank	Pottery clay
Clay Spike No. 1	Pottery clay, spiked with selected PCDD's and PCDF's
Clay Spike No. 2	Pottery clay, spiked with selected PCDD's and PCDF's
Sludge Blank	Sludge from industrial PCP process
Sludge Spike No. 1	Sludge Blank, spiked with selected PCDD's and PCDF's
Sludge Spike No. 2	Sludge Blank, spiked with selected PCDD's and PCDF's.

The results obtained by Lockheed-EMSCO personnel familiar with the Method,

although not obtained as part of the blind study, are valuable for comparison and are included in the relevant Tables.

A very simple, qualitative measure of how well the combined extraction, chromatographic cleanup, and GC/MS analysis prescribed in the Method deals with the various analytes may be obtained by noting the number of the specified analytes for which values were reported by each laboratory. As shown in Table 7-1, at least one laboratory in addition to LEMSCO detected all of the analytes, and two laboratories reported on 32 of 38. Relatively lower reporting by Laboratories II and IV (total: 49 of 76) is presumed to be due to lack of familiarity with the extraction and cleanup procedures and may be expected to improve with experience.

A more quantitative measure of the extraction and cleanup efficiency is provided by monitoring the percent recovery of the internal standard ($^{13}C_{12}$-2,3,7,8-TCDD) which was added to the sample immediately prior to extraction. Table 7-2 shows that three of the participating laboratories, apart from LEMSCO, obtained acceptable results (mean recovery greater than 40 percent). The two other laboratories reported mean recoveries of less than 30 percent.

Individual results for the 13 analytes spiked into Clay Spike No. 1 and No. 2 and for the 6 analytes spiked into Sludge Spike No. 1 and No. 2 are shown in Tables 7-3 and 7-4, respectively.

The mean value for 114 determinations of 11 analytes spiked into clay at the 5 ppb level was 6.02 ± 2.78 ppb.

The mean value for 16 determinations of 2 analytes spiked into clay at the 2.5 ppb level was 3.56 ± 2.35 ppb.

The mean value for 57 determinations of 6 analytes spiked into sludge at the 125 ppb level was 126.4 ± 57.9 ppb.

The accuracy and bias of these determinations of analytes spiked into clay at 2.5 ppb and 5.0 ppb and spiked into sludge at 125 ppb are calculated as follows:

$$\text{Accuracy} = \left(\frac{\text{Mean Measured Value}}{\text{True Value}}\right) \times 100\%$$

$$\text{Bias} = (\text{Accuracy} - 100)\ \%$$

$$\text{Standard Deviation (SD) of Bias Estimate} = \left(\frac{\text{SD of Mean Measured Value}}{(\text{Number of Determinations})^{1/2}} \times \frac{1}{\text{True Value}}\right) \times 100\%$$

and are shown in Table 7-5.

TABLE 7-1. INTERLABORATORY TEST OF METHOD 8280, PHASE I:
SUMMARY OF ANALYTES REPORTED BY PARTICIPATING LABORATORIES

Sample	Number of Analytes Spiked	Number of Analytes Reported by Each Laboratory					
		LEMSCO	I	II	III	IV	V
Clay Spike No. 1	13	13	13	8	12	11	12
Clay Spike No. 2	13	13	13	8	12	4	12
Sludge Spike No. 1	6	6	6	3	4	6	4
Sludge Spike No. 2	6	6	6	3	4	6	4

TABLE 7-2. INTERLABORATORY TEST OF METHOD 8280, PHASE I: PERCENT RECOVERY OF INTERNAL STANDARD $^{13}C_{12}$-2,3,7,8-TCDD

Sample	LEMSCO	Participating Laboratories I	II	III	IV	V	Mean	RSD Percent
Clay Blank	66.3	34.3	9.1	54	21	67	42.0	57.7
Clay Spike No. 1	62.8	64.3	13.3	53	26	63	47.1	46.7
Clay Spike No. 2	78.9	132	10.2	60	14	58	58.9	76.4
Sludge Blank	88.4	84.5	28.7	57	34	35	54.6	48.6
Sludge Spike No. 1	66.1	79.0	28.4	12	25	32	40.4	64.6
Sludge Spike No. 2	74.0	96.4	32.9	15	36	44	49.7	60.2

TABLE 7-3. INTERLABORATORY TEST OF METHOD 8280, PHASE I: QUANTITATION OF ANALYTES IN SPIKED CLAY SAMPLES (PPB)

Analyte	Spike Level	Participating Laboratories							
		LEMSCO	I	II	III	IV	V	Mean	RSD Percent
2,3,7,8-TCDD	5.0	4.87	9.54	4.9	4.29	3.9	9.3	6.52	42.9
		5.15	12.4	5.4	4.27	ND	7.7		
1,2,3,4-TCDD	5.0	3.52	7.88	6.6	4.00	4.1	8.3	5.86	97.8
		3.67	5.58	9.2	4.10	ND	7.5		
1,3,6,8-TCDD	2.50	2.11	5.40	2.65	ND	--[a]	3.0	3.42	45.6
		2.11	2.18	6.1	ND	--[a]	3.8		
1,3,7,9-TCDD	2.50	2.26	4.0	6.4	0.54	--[a]	--[a]	3.70	82.7
		2.18	3.92	9.6	0.68	--[a]	--[a]		
1,3,7,8-TCDD	5.0	4.88	10.8	12.8	2.61	3.0	9.7	8.11	63.1
		5.00	10.8	19.0	2.77	ND	7.9		
1,2,7,8-TCDD	5.0	4.16	10.3	4.4	3.90	3.8	6.9	5.81	41.8
		4.58	9.74	4.7	3.86	ND	7.6		
1,2,8,9-TCDD	5.0	4.32	6.83	ND	4.26	5.7	7.5	5.63	26.8
		4.51	5.29	ND	4.17	ND	8.1		
1,2,3,4,7-PeCDD	5.0	4.40	7.89	0.3	3.20	6.0	6.6	4.82	58.5
		4.56	9.61	0.3	3.29	4.7	7.0		
1,2,3,7,8-PeCDD	5.0	5.48	9.45	ND	3.65	8.5	7.9	6.69	34.5
		5.22	5.58	ND	3.88	6.8	10.4		
1,2,3,4,7,8-HxCDD	5.0	5.25	9.58	ND	2.64	6.1	7.3	5.91	42.3
		5.29	4.83	ND	2.80	29.0[b]	9.4		
1,2,7,8-TCDF	5.0	4.64	7.80	3.3	4.17	4.8	9.3	5.39	39.0
		4.63	4.87	3.1	4.29	ND	8.4		
1,2,3,7,8-PeCDF	5.0	4.82	8.07	ND	3.88	5.0	8.4	5.74	33.1
		4.94	4.76	ND	3.65	ND	8.1		
1,2,3,4,7,8-HxCDF	5.0	4.70	7.83	ND	1.78	5.8	8.1	5.79	47.8
		4.90	4.03	ND	2.13	9.6	9.0		

[a]Not determined.
[b]Not included in calculation of mean and standard deviation.
ND = Not detected.

TABLE 7-4. INTERLABORATORY TEST OF METHOD 8280, PHASE I: QUANTITATION OF ANALYTES IN SPIKED SLUDGE SAMPLES (PPB)

Analyte	Spike Level	LEMSCO	Participating Laboratories I	II	III	IV	V	Mean	RSD Percent
2,3,7,8-TCDD	125.0	132.1 127.9	62.2 48.9	156.4 153.2	270 220	150 155	163.2 184.8	152.0	39.4
1,3,7,8-TCDD	125.0	147.3 134.5	50.7 29.1	204.2 185.1	ND ND	93 84	177.9 116.1	122.2	47.8
1,2,7,8-TCDD	125.0	132.2 128.5	85.7 38.3	181.6 173.5	50 37	180 160	ND ND	116.7	50.8
1,2,8,9-TCDD	125.0	136.4 135.6	60.9 33.7	ND ND	160 140	260 180	805.2[a] 205.6	145.8	47.3
1,2,3,4,7-PeCDD	125.0	113.3 118.8	67.2 42.4	ND ND	87 68	110 140	ND ND	93.3	34.9
1,2,3,7,8-PeCDF	125.0	115.1 123.4	48.2 33.4	ND ND	ND ND	120 150	170.9 171.7	116.6	44.4

[a]Not included in calculation of mean and standard deviation.
ND = Not detected.

TABLE 7-5. INTERLABORATORY TEST OF METHOD 8280, PHASE I: ACCURACY AND BIAS OF RESULTS

Sample Type	Spike Level (ppb)	Number of Determinations	Accuracy (Percent)	Bias (Percent)	± SD of Bias Estimate
Clay	2.5	16	142.4	+ 42.4	± 11.8
Clay	5.0	114	120.4	+ 20.4	± 5.21
Sludge	125	57	101.1	+ 1.12	± 6.14

COMMENTS FROM LABORATORIES ON PHASE I OF INTERLABORATORY STUDY

LABORATORY I

None

LABORATORY II

1. Standards that were provided for calibration were at a concentration level that did not allow the highest concentration requested to be analyzed without further concentration of the solution.

   Analytical standards provided with Phase II of the Interlaboratory Study will be at a concentration in the range 10 to 50 ng/µL. It will therefore not be necessary to concentrate the standards for the initial calibration.

2. Internal standard ($^{13}C_{12}$-2,3,7,8-TCDD) recovery for all samples was noted to be extremely low. This should be investigated before any further work is attempted.

   The Method has been shown to routinely provide recoveries greater than 60 percent. A summary of results provided by the other participating laboratories is included in this report.

3. The cleanup of samples after extraction seems tedious when compared with Dioxin-IFB procedures. The use of concentrated sulfuric acid presents a safety problem and in the case of sludge samples required seven rinses to remove all color.

   The Dioxin-IFB method requires determination only of 2,3,7,8-TCDD. The sulfuric acid wash is necessary for certain sample matrices, e.g., industrial sludges, still bottoms, sawdust, etc., which contain high levels of interferences. The revised Method requires a maximum of four acid washes. Appropriate care should be exercised.

LABORATORY III

1. The selection of internal standards must be improved. At a minimum, we feel that $^{13}C_{12}$-TCDD, $^{13}C_{12}$-OCDD, and $^{13}C_{12}$-TCDF should be used. As standards become more available, the goal should be to have an internal standard for each congener level (true isotope dilution technique).

   Agreed; the OCDD isomer is now included in the Method, and the use of other isomers was referenced in previous versions as well as in the current edition.

2. We feel $^{13}C_{12}$-1,2,3,4-TCDD is a poor choice as the recovery standard because it can swamp the 2,3,7,8-TCDD internal standard response on a DB-5 column. An isomer with better separation from 2,3,7,8-TCDD should be selected.

   Baseline resolution of the internal and recovery standards would certainly be preferable; however, to our knowledge, no other $^{13}C_{12}$-TCDD is available. The internal standard response can be swamped when poor recoveries from the cleanup step are obtained.

3. The DFTPP requirement is totally useless; it has nothing to do with Cl_4-Cl_8 selected ion monitoring analyses. As an alternative, we would suggest calibrating the instrument using FC-43, then using mass-ratio windows as acceptance of instrument tune and peak identification.

   Agreed. The revised version of Method 8280 deletes the DFTPP tune requirement and substitutes criteria based on mass calibration over the range m/z 222-506 using perfluoro-tri-n-butylamine (FC-43).

4. Use tetradecane as a keeper instead of the "just to dryness" technique.

   Agreed, the use of an appropriate "keeper" would be preferable.

5. Use tetradecane as solvent for the final extract. This reduces volume changes and makes it much more accurate to specify exact final volumes (e.g., 100 µL, 50 µL, 10 µL).

   Tetradecane may be used as the final solvent, as noted in the procedure. For the purposes of this study, toluene is recommended.

6. Make the final volume for all matrix types 50 µL. This would increase the absolute response of internal standards and require less recovery standard.

   To require a 50 µL final volume for all sample types may require very small sample size for high-level samples. The response of internal standards is adequate provided the extraction/cleanup procedure is performed efficiently. It is difficult to concentrate accurately to low volumes, and it is not recommended.

7. For highly organic sludge samples, we would suggest adjusting the extract after roto-evaping to 5 mL with hexane, then proceeding to the cleanup step with only 1 mL of the extract. This reduces by 80 percent the organic matrix that tends to overload the columns and alter elution profiles to the point where internal standard recoveries are affected.

   Although this would remove much of the organic interferences, it would also of course remove 80 percent of the analytes of interest. In addition, 80 percent of the expensive $^{13}C_{12}$-labeled standards would also be discarded. Spiking with five times the normal level of $^{13}C_{12}$-standards would probably be prohibitively expensive.

8. We prepared charcoal packing using their AX-21, but substituted Kieselgel 60 for Spherisorb.

   The Spherisorb S10W is currently $75/10g. Our testing indicates that less expensive silica gel can be substituted without a great difference in results.

9. We could not set up and operate the pressurized charcoal column as described. Instead, we used our own (gravity-flow) procedure.

   We are investigating this problem and expect that gravity-flow columns may be recommended in the future; meanwhile, this procedure will require the use of pressurized columns.

LABORATORY IV

1. The use of $^{13}C_{12}$-TCDD recovery and internal standards should give excellent quantitation with good recoveries. A $^{13}C_{12}$-octachlorodibenzo-p-dioxin spike could (should) be used to monitor recoveries over the range of chlorination from 4 chlorines to 8 chlorines. This would assure that fractionation within the range of compounds was not occurring during sample cleanup.

   Agreed; the documentation for this study will require $^{13}C_{12}$-OCDD to be spiked as an additional internal standard.

2. The LC-carbon cleanup requires almost 2 hours per sample. This same column material is being used by the Bay St. Louis EPA Laboratory in a disposable pipette. One obvious advantage is that 6 to 8 samples can be processed at one time where this is impractical with the LC.

   The EPA Bay St. Louis carbon column uses AX-21 mixed with 200 to 300 µm silica gel for faster flow rates. Recoveries of tetra- through octa-CDD's/CDF's are, reportedly, very good. This procedure may be recommended in future.

3. The concentration of the 1368/1379-TCDD standard was not well defined. The two isomers were excluded from our analysis since reliable response factors could not be determined.

1,3,6,8- and 1,3,7,9-TCDD were each spiked at 2.5 ppb by error; this requirement has been removed from this phase of the study.

4. A Soxhlet extractor procedure with solvents such as benzene has been demonstrated to work well as the initial means of separation. The petroleum ether/methanol extraction of clay looks weak.

   A Soxhlet procedure may require as much as 16 hours per extraction, and benzene is not a recommended solvent because of its toxicity/carcinogenicity; toluene would be an acceptable substitute. This procedure is included as an acceptable method of extraction.

5. We have routinely done CDD's in a variety of samples for the past 10 years. This is the worst set of recoveries I have ever seen. The step where the analyte has been lost needs to be found and the procedure modified to correct the recovery problem.

   The Method has been shown to routinely provide recoveries greater than 70 percent. A summary of results provided by the other participating laboratories is included in this report.

6. Isotope dilution (mass spectrometry) has been used since the late 1930's, for inorganic compounds in more recent times. Two complications relative to this technique should be mentioned.

   a. When the ratio of labeled compounds to analyte is large or when the ratio of analyte to labeled compound is large, the accuracy and precisions are decreased through error propagation. The minimum error occurs when the ratio is 1:1.

   b. When different types of compounds are being quantitated relative to the internal standard, the method is basically an internal standard method. It works only as long as pre-separation of the analytes has not occurred.

      a. Agreed.

      b. Agreed.

      We recognize that this laboratory recommends the use of external standard quantitation. However, that procedure is not to be used in this method.

LABORATORY V

1. Some of the terminology relating to the standards is confusing and, in at least one instance of what is printed in the Method, wrong. The use of the term "internal standard" can be totally confusing. At one point in the method, the compound relative to which response factors are calculated and relative to which the quantities of analyte are calculated is referred to as the "internal standard." Then, at a later point in the procedure, the "internal standard" is described as the compound added shortly before

analysis and, at another point, the "internal standard" is the compound added at the start of the extraction procedure. In my laboratory, we have removed any confusion by referring to the "Quantitation Standard" and the surrogate compound. We don't use the term "internal standard" at all. The Quantitation Standard is the basis for all quantitative calculations.

The compound added at the start of the extraction procedure and referred to as the internal standard is $^{13}C_{12}$-2,3,7,8-TCDD. This is the same compound relative to which response factors are calculated and against which analytes are quantitated. Use of the term "internal standard" is therefore accurate and self-consistent. The compound added to the extract shortly before GC/MS analysis is not referred to as the internal standard; it is a different compound ($^{13}C_{12}$-1,2,3,4-TCDD), it is referred to as the recovery standard and is the compound against which the recovery of the internal standard is quantitated.

2. We found the 200 ng/mL calibration standard to be below our quantifiable limit. We could not get good reproducible results for the calibration standard at this level. The extracted ion current profiles for the masses of interest are jagged peaks near the noise level of the instrument at this concentration, and we did not feel that we could validly use the information from this calibration sample in performing our quantitative calculations. Perhaps the method ought to provide for this contingency with the option of discarding this lower point or of raising the concentration in order to generate a valid data point.

   Samples containing dioxins/furans at low levels need a calibration standard at this level for accurate quantitation. If 200 ng/mL is too low to be accurately quantitated, then instrument sensitivity should be improved by cleaning ion source or rods or both, replacing the GC column, etc.

3. The criterion of 10 percent for the relative abundances of ions in any given isotope cluster is not realistic. I'm not sure just where it ought to be set (or, indeed, if this type of criterion ought to be set at all). We encountered a range of variation greater than 10 percent in going through the concentration range of our calibration samples (see the tables with the clay soil results). This variation might be due to a number of reasons, but at least in the calibration standards, one is certain of the compound identifications and if the criterion cannot be met across a concentration range, the criterion is unrealistic.

   The criterion of relative ion abundances being within ±10 percent of the theoretical values is readily achieved, even with very low level calibration standards. The allowable error has been increased to ±15 percent in the revised Method. A relative abundance criterion is necessary because of potential, co-eluting interferences, e.g., chlorinated diphenyl ethers.

4. Setting a criterion of satisfying DFTPP tuning requirements for this analysis is the height of idiocy and probably contributes significantly to problems No. 2 and 3. The lowest mass of interest in this entire assay is mass 306. Thus, all of the DFTPP peaks below mass 300 are irrelevant and tuning to have the correct mass balance for the masses below 100 incurs substantial costs in overall sensitivity. It would make far more sense to tune the quadrupole mass spectrum for resolution and optimum sensitivity, with good peak shape for the higher masses of the calibration standard. Tuning in this manner would enhance sensitivity for the higher masses to lower LODs.

   Agreed. The revised version of Method 8280 deletes the DFTPP tune requirement and substitutes criteria based on mass calibration over the range m/z 222-506 using perfluorotri-n-butylamine (FC-43).

5. A blanket requirement to generate confirmatory mass spectra using peak top enhancement may also produce false negatives, since sometimes the best spectra are produced by enhancement and sometimes the best spectra are produced by manual averaging with specific background subtraction. The operator should be left with discretion in this area.

   There is no such requirement in the Method.

6. The exact technique used for final volume adjustment of samples appears to be critical in determining even whether quantitation standard will be observed. There is a very real tendency for the analyte to cling to the glass walls, so a concentration technique which ensures that the analyte is not blown toward the vessel walls is really important. Also, our experience is that toluene is the solvent of choice for the calibration samples. We had problems with observing the compounds in methylene chloride.

   The concentration step is indeed critical. Vials should be silanized prior to use to minimize the tendency of analytes to cling to the glass walls. Only a very gentle stream of nitrogen should be used in the blow-down step. To our knowledge, no other concentration method is available. Toluene is the solvent of choice: the calibration standards were not provided in methylene chloride.

7. It should be stressed in the method that it is extremely important to do a thorough filtration (with copious solvent rinses) to remove particulate materials. The presence of particulate materials produces terrible emulsions in subsequent separation steps, with associated loss of analyte.

   Samples containing large amounts of particulate matter should have the acid washes performed first. This will greatly reduce the problem of particulates in the filtrate. Thorough rinsing of the filter with solvent is of course important. It is almost impossible to prevent the formation of emulsions in very dirty samples.

8. It is also critical to pre-test the column chromatography with standards in order to monitor exactly which fraction to analyze. The method states

that a certain elution fraction will contain the analyte, but exactly which fraction contains the analyte and whether it is appropriate to combine certain fractions in order to obtain the best yield of surrogate can only be determined for a given batch of alumina by performing a preliminary test.

Of course the column chromatography should be pre-tested using tetra- through octa-calibration standards, as specified in the Method (Section 6.1). To combine fractions from the alumina column defeats the purpose of the column. Alumina which is kept properly conditioned should require very little change in the composition of the methylene chloride/hexane fraction.

PHASE II

The objective of Phase II of the interlaboratory study was to test the applicability of the Method to the analysis of samples which were much more difficult and complex than those used for Phase I. Significant revisions to the Method were made between completion of Phase I and initiation of Phase II. These revisions were made to several critical areas, including:

- Multiple ion detection descriptors
- Carbon column cleanup
- Sample/final extract size
- Analytes to be quantitated
- DB-5 GC column requirement
- Deletion of DFTPP tune requirement
- Insertion of perfluoro-tri-n-butylamine (FC-43) tune requirement
- Sample reanalysis requirements based on recovery criteria for the internal standards.

Further, these revisions were based both on our own laboratory experiences and on the comments/suggestions provided by the participating laboratories at the conclusion of Phase I. The same five laboratories which took part in Phase I also collaborated in Phase II, and each was provided with identical packages of samples, analytical standards and documentation etc., similar to those provided for Phase I. Each laboratory was requested to analyze a total of 10 samples of 4 different sample types. As in Phase I, duplicate samples of each sample type were provided to check accuracy and precision. In addition, a third different sample of each of two sample types was also to be analyzed. The greatest difference between the requirements for Phase I and Phase II was in which analytes were to be quantitated. Whereas Phase I required the determination of certain selected CDD's and CDF's, the Method was tested under Phase II for the quantitation of total tetra- through octa-CDD's and CDF's. This change as specified

in the Method presented some difficulties in view of the use of different MID descriptors at different points along the GC elution profile. It is appreciated that not all of the isomers within a given series may be detected using this procedure. For instance, at least five early-eluting PeCDD isomers will probably overlap the late-eluting TCDD/TCDF isomers. Similar overlap may occur between the penta-, hexa-, and hepta-congener groups. However, the chromatographic windows prescribed here were developed within the limitations of the PCDD/PCDF standards available to this laboratory during the course of this study. It is expected that, as additional reference standards become available, chromatographic conditions will be refined accordingly.

However, to ensure standardization amongst the laboratories for the purposes of this study, explicit instructions regarding change-over points of the MID descriptors were provided.

Each laboratory was provided with a set of the following 10 samples which had been analyzed by Lockheed-EMSCO. The samples were all hazardous waste samples provided by the EPA and had not been spiked with PCDD's/PCDF's in contrast to the samples used for Phase I.

Sample No.	Type	Sample No.	Type
1,2	Fly-ash duplicates	6	Sludge A
3	Soil A	7,8	Sludge B duplicates
4,5	Soil B duplicates	9,10	Still-bottom duplicates

Data packages from the six laboratories were audited with an emphasis on Method performance. The data were entered into a spreadsheet to facilitate comparison and evaluation. In those instances where a large difference occurred among the values reported for a particular sample, the raw data were examined to try to determine if the difference was a Laboratory problem or a Method problem. Laboratory II evidenced analytical problems due to errors or not following instructions which affected their results for all of the samples. Only one-fifth the required amount of internal standard was added; this resulted in extremely low internal standard responses and biased quantitation. Because of these problems, it was recommended that the data from this laboratory be excluded from the statistical analysis as not being representative of Method performance. Problems with individual data points were also examined and were traced to a variety of causes. Calculation and data transposition errors were found; other discrepancies were traced to differences in instrument sensitivity, to differences in retention-time windows scanned, and to isomer peaks which met identification criteria in one laboratory and not in others. The data reported are summarized in Tables 7-6 through 7-13; although the data from Laboratory II were excluded from the statistical analysis for the reasons cited above, they are included in these Tables for completeness.

In general, the Method performed well when the laboratories followed the protocol. A visual examination of the data showed that approximately 85 percent of the values reported by the 5 laboratories and used in the statistical analysis were consistent among the laboratories.

TABLE 7-6. INTERLABORATORY TEST OF METHOD 8280, PHASE II: PERCENT RECOVERY OF INTERNAL STANDARD $^{13}C_{12}$-2,3,7,8-TCDD

		Participating Laboratories					All Results		Excluding Lab II Results	
Sample	LEMSCO	I	II	III	IV	V	Mean	RSD Percent	Mean	RSD Percent
Fly-Ash*	89.8	103	98.1	59	64	101	85.1	23.5	82.1	25.2
	81.1	98	102	60	56	109				
Soil A	74.4	42.3	53.6	53.6	46	75	57.5	24.3	58.3	26.7
Soil B*	67.2	54.3	50.0	51	42	90	58.8	25.2	59.4	27.1
	62.2	54.3	62	45	46	82				
Sludge A	64.9	77.7	40.6	18	33	74	51.4	47.3	53.5	49.6
Sludge B*	53.8	78.7	40.9	69	72	72	63.4	26.1	67.1	23.1
	41.9	84.1	48.9	51	58	90				
Still-Bottom*	72.6	118	61.9	74	46	104	72.9	35.2	73.5	38.1
	84.8	23	78.3	69	53	90.5				

*Blind duplicates.

TABLE 7-7. INTERLABORATORY TEST OF METHOD 8280, PHASE II: PERCENT RECOVERY OF INTERNAL STANDARD $^{13}C_{12}$-OCDD

		Participating Laboratories					All Results		Excluding Lab II Results	
Sample	LEMSCO	I	II	III	IV	V	Mean	RSD Percent	Mean	RSD Percent
Fly-Ash*	75.5	98	90	34	64	102	74.0	33.5	74.8	36.7
	78.1	119	50	38	56	83				
Soil A	46.2	53	65	29	43	112	58.0	49.9	56.6	56.8
Soil B*	68.1	87	3.2	14	95	150	63.6	71.6	75.4	53.1
	67.3	67	5.8	29	58	119				
Sludge A	55.5	75	0[a]	37	40	46	50.7	30.2	50.7	30.2
Sludge B*	47.3	145	23	50	75	74	61.0	65.4	68.6	57.8
	39.2	132	24	28	48	47				
Still-Bottom*	96.4	180	0[a]	32	58	55	69.5	71.3	69.5	71.3
	125	30.8	0[a]	33	46	39				

[a]Not included in calculation of mean and standard deviation.
*Blind duplicates.

TABLE 7-8. INTERLABORATORY TEST OF METHOD 8280, PHASE II: QUANTITATION OF TOTAL DIOXINS AND DIBENZOFURANS IN FLY-ASH (PPB)

Analyte	LEMSCO	Participating Laboratories I	II	III	IV	V	All Results Mean	All Results RSD Percent	Excluding Lab II Results Mean	Excluding Lab II Results RSD Percent
TCDD	106	87.3	51	150	66	81	91	37.6	100	30.7
	97	78.7	44.6	116	66	148				
PeCDD	136	196	14.4	201	55	231	131	64.8	150	52.9
	108	212	58.1	94.4	16	248				
HxCDD	215	300	170	391	230	330	249	32.8	264	30.9
	217	136	176	324	170	323				
HpCDD	116	128	135	417	150	262	236	50.1	228	48.7
	102	250	415	295	180	377				
OCDD	55	209	191	160	100	186	170	80.8	171	88.5
	50	159	137	124	92	574				
TCDF	215	73.9	ND	281	150	115	179	43.3	179	43.3
	203	89.6	ND	219	140	301				
PeCDF	138	148	14.4	223	96	175	121	51.6	139	35.8
	130	129	45.3	86.6	67	201				
HxCDF	65	53.6	24.8	148	50	113	73	58.7	83	46.2
	89	44	15.2	107	37	123				
HpCDF	24	53.2	47.2	119	380	67	96	99.7	101	103.4
	22	49.8	97.4	82	130	79				
OCDF	7	ND	16.4	26.6	16	5	14	48.7	14.1	53.8
	6	17.7	14.6	19.3	9	20				

TABLE 7-9. INTERLABORATORY TEST OF METHOD 8280, PHASE II: QUANTITATION OF TOTAL DIOXINS AND DIBENZOFURANS IN SOIL A (PPB)

Analyte	LEMSCO	Participating Laboratories					All Results		Excluding Lab II Results	
		I	II	III	IV	V	Mean	RSD Percent	Mean	RSD Percent
TCDD	395	712	470.6	674	480	764	583	26.1	605	26.3
PeCDD	ND	ND	ND	ND	14	ND	14	--	14	--
HxCDD	ND	ND	ND	ND	ND	ND	ND	--	ND	--
HpCDD	ND	ND	20.7	ND	27	ND	24	18.7	27	--
OCDD	5	3.51	141.1	ND	140	ND	72	108.7	50	158.3
TCDF	31	31.6	38.4	49.3	32	54	39.4	25.3	39.6	28.2
PeCDF	ND	ND	ND	4.1	ND	4	4.1	1.7	4.1	1.7
HxCDF	ND	ND	ND	ND	ND	ND	ND	--	ND	--
HpCDF	ND	ND	2.6	ND	ND	ND	2.6	--	ND	--
OCDF	ND	ND	7.1	ND	ND	ND	7.1	--	ND	--

TABLE 7-10. INTERLABORATORY TEST OF METHOD 8280, PHASE II: QUANTITATION OF TOTAL DIOXINS AND DIBENZOFURANS IN SOIL B (PPB)

Analyte	LEMSCO	Participating Laboratories I	II	III	IV	V	All Results Mean	All Results RSD Percent	Excluding Lab II Results Mean	Excluding Lab II Results RSD Percent
TCDD	2	ND	ND	ND	ND	ND	2	0	2	0
	2	ND	ND	ND	ND	ND				
PeCDD	ND	7.17	4	4.6	5.1	ND	3.9	47.1	4.3	48.6
	ND	2.17	2.3	ND	2.3	ND				
HxCDD	265	427	230	430	360	333	363	26.0	385	22.5
	330	456	277	298	560	389				
HpCDD	2,974	3210	194	9480	2450	3254	3463	68.2	4114	48.6
	2,989	3930	224	3990	4500	4365				
OCDD	7,550	ND	94.2	6880	6800	45174	12235	121.7	15271	99.8
	7,229	ND	88.5	6310	8500	33726				
TCDF	15	ND	0.6	6.5	9.8	ND	7.6	89.9	9.3	69.9
	22	0.85	0.4	5.2	7.3	8				
PeCDF	19	51	53	66	120	53	118	169.0	133	165.3
	ND	50.3	50.4	60.2	715	62				
HxCDF	510	333	344	777	630	475	484	32.5	513	30.5
	423	409	331	553	715	308				
HpCDF	725	627	67.2	2750	620	612	805	85.0	951	68.9
	706	578	78.9	1100	1000	794				
OCDF	523	626	9.4	1140	470	1166	649	61.5	777	37.7
	506	772	7.9	557	800	1205				

TABLE 7-11. INTERLABORATORY TEST OF METHOD 8280, PHASE II: QUANTITATION OF TOTAL DIOXINS AND DIBENZOFURANS IN SLUDGE A (PPB)

Analyte	LEMSCO	Participating Laboratories					All Results		Excluding Lab II Results	
		I	II	III	IV	V	Mean	RSD Percent	Mean	RSD Percent
TCDD	6	ND	ND	ND	ND	ND	6	--	6	--
PeCDD	ND	181	ND	431	77	ND	230	79.2	230	79.2
HxCDD	1741	2150	986	6970	3520	768	2689	86.1	3030	79.7
HpCDD	15743	12500	337	14500	2200	6348	8605	76.3	10258	56.3
OCDD	19013	18400	42.1	12900	14000	52912	19545	90.7	23445	71.2
TCDF	23	7.26	ND	ND	ND	ND	15	73.6	15	73.6
PeCDF	1	67.1	ND	ND	33	ND	34	98.1	34	98.1
HxCDF	52	99.3	47.8	622	270	48	190	120.2	218	111.5
HpCDF	400	174	4.4	304	300	ND	237	64.5	295	31.4
OCDF	60	88.6	ND	110	100	271	126	66.0	126	66.0

TABLE 7-12. INTERLABORATORY TEST OF METHOD 8280, PHASE II: QUANTITATION OF TOTAL DIOXINS AND DIBENZOFURANS IN SLUDGE B (PPB)

Analyte	LEMSCO	Participating Laboratories I	II	III	IV	V	All Results Mean	All Results RSD Percent	Excluding Lab II Results Mean	Excluding Lab II Results RSD Percent
TCDD	10	ND	ND	ND	ND	ND	10	--	10	--
	ND	ND	ND	ND	ND	ND				
PeCDD	ND	ND	ND	42.5	ND	ND	36	24.3	36	24.3
	ND	ND	ND	30	ND	ND				
HxCDD	353	444	234	604	320	708	399	39.7	433	34.7
	356	310	216	607	306	326				
HpCDD	1582	1590	155	2400	110	1748	1426	69.7	1673	53.4
	1494	450	228	2460	3100	1797				
OCDD	2588	3800	253	3160	2950	11403	3741	77.4	4426	60.3
	2911	3080	386	3290	5300	5774				
TCDF	69	82.1	45.1	93.3	ND	27	61	45.7	70	30.2
	78	ND	9.3	77.7	ND	64				
PeCDF	6	56.7	21	120	ND	54	61	77.6	66	72.6
	28	35.6	ND	148	ND	82				
HxCDF	491	9.67	179	694	380	552	402	55.9	451	47.3
	471	237	134	744	410	523				
HpCDF	457	130	446	716	360	627	467	52.4	512	44.0
	411	295	40.8	781	830	508				
OCDF	98	ND	7.8	145	76	31	91	81.8	109	63.7
	94	97.9	8.2	147	260	36				

TABLE 7-13. INTERLABORATORY TEST OF METHOD 8280, PHASE II: QUANTITATION OF TOTAL DIOXINS AND DIBENZOFURANS IN STILL-BOTTOM (PPB)

Analyte	LEMSCO	Participating Laboratories I	II	III	IV	V	All Results Mean	All Results RSD Percent	Excluding Lab II Results Mean	Excluding Lab II Results RSD Percent
TCDD	1210	3280	553	1300	640	1600	1415	56.7	1563	51.9
	1443	ND	948	1790	640	2160				
PeCDD	ND	ND	17.7	330	ND	ND	280	66.7	367	22.1
	ND	ND	ND	311	460	ND				
HxCDD	1771	ND	ND	ND	95	ND	933	127	933	127.0
	ND	ND	ND	ND	ND	ND				
HpCDD	ND	ND	ND	ND	ND	ND	440	--	440	--
	ND	ND	ND	ND	440	ND				
OCDD	ND	ND	ND	ND	760	ND	1810	82	1810	82.0
	ND	ND	ND	ND	2860	ND				
TCDF	269[a]	246[a]	112[a]	279[a]	240[a]	294[a]	238[a]	25.7	260[a]	13.8
	245[a]	310[a]	144[a]	260[a]	180[a]	275[a]				
PeCDF	181[a]	337[a]	399[a]	191[a]	185[a]	314[a]	211[a]	44.4	206[a]	32.7
	166[a]	143[a]	70[a]	178[a]	141[a]	222[a]				
HxCDF	16[a]	2320	237	13[a]	14[a]	26[a]	9.7[a]	83.7	11.5[a]	69.2
	16[a]	1160	253	12[a]	848	14[a]				
HpCDF	ND	5450	119	8650	4720	11245	5116	68.3	6.3[a]	42.9
	ND	3410	456	8100	4070	4940				
OCDF	ND	2800	54.1	1850	1050	ND	1110	78.6	1.4[a]	54.7
	ND	810	162	1700	720	840				

[a]ppm

STATISTICAL ANALYSIS OF DATA FROM PHASE II OF INTERLABORATORY STUDY

The following three statistical tests were applied:

Test A — to see if the mean recovery of each internal standard is a function of sample type

Test B — to see if the laboratories are equivalent in accuracy (mean analytical value) for any of the 10 analytes

Test C — to see if the laboratories are equivalent in precision (variance of mean analytical value) for any of the 10 analytes

The data used were those reported by five laboratories (LEMSCO, I, III, IV, V). Data from Laboratory II were excluded because the internal standards were added at only one-fifth of the level required; this resulted in very low area counts. All calculations were performed on a IBM PC/XT computer using a Lotus-123 worksheet written specifically for this application.

Test A was performed using one-way analysis of variance, and the results are presented in Table 7-14 for $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-OCDD. The results show that there appears to be an effect due to sample type for $^{13}C_{12}$-2,3,7,8-TCDD but not for $^{13}C_{12}$-OCDD. In other words, $^{13}C_{12}$-2,3,7,8-TCDD recovery depends on sample type whereas $^{13}C_{12}$-OCDD recovery does not.

Test B was performed using two-way analysis of variance. Analytical values reported as "Not Detected" were considered to be zero for the purposes of this statistical analysis and were disregarded. The results, presented in Table 7-15, show that significant differences among laboratory means were found only for OCDD. The other analytes do not exhibit significant evidence of interlaboratory variation of the mean.

Test C was performed using Cochran's test for homogeneity of variance. The data used were the analytical values reported for the blind duplicate samples (soil, fly-ash, still-bottom, and sludge), and the results are presented in Table 7-16. As the Table shows, 9 of the 40 possible matrix/analyte combinations exhibited significant evidence of unequal variances among the 5 laboratories. The other 31 combinations showed no such evidence, but it should be noted that several had insufficient data due to "Not Detected" analytical values.

It should be further noted that equivalency of variances was assumed in Test B. In view of the results of Test C, the significance level indicated in Test B should be considered approximate only. Fortunately, each of the F-ratios in Test B was either not significant (probability > 0.05) or was highly significant (probability < 0.01), with none being moderately significant ($0.05 >$ probability > 0.01). Thus the results of Test B are valid.

TABLE 7-14. STATISTICAL TEST A: ANALYSIS OF VARIANCE OF RECOVERY OF INTERNAL STANDARDS

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio
		$^{13}C_{12}$-2,3,7,8-TCDD		
Samples	3	3,905.8	1,301.9	3.02*
Error	46	19,816.2	430.8	
Total	49	23,722.0		

*Significant at 5 percent level ($\alpha = 0.05$).

		$^{13}C_{12}$-OCDD		
Samples	3	919.3	306.4	0.22
Error	46	65,054.2	1,414.2	
Total	49	65,973.5		

TABLE 7-15. STATISTICAL TEST B: LABORATORY EQUIVALENCY
(TWO-WAY ANALYSIS OF VARIANCE ON MEANS)

Analyte	Degrees of Freedom				F-Ratios	
	Samples	Labs.	Error	Total	Samples	Labs.
TCDD	9	4	36	49	753*	0.65
PeCDD	9	4	36	49	197*	1.95
HxCDD	9	4	36	49	485*	0.95
HpCDD	9	4	36	49	1,006*	1.38
OCDD	9	4	36	49	426*	4.39*
TCDF	9	4	36	49	17,877*	1.30
PeCDF	9	4	36	49	4,595*	1.21
HxCDF	9	4	36	49	868*	1.94
HpCDF	9	4	36	49	692*	2.44
OCDF	9	4	36	49	409*	1.58

*Significant at 1 percent level ($\alpha = 0.01$).

TABLE 7-16. STATISTICAL TEST C: LABORATORY EQUIVALENCY
(COCHRAN'S TEST FOR EQUAL VARIANCES)

Matrix	Analyte	Cochran's G-Statistic	Laboratory with Largest Variance
Soil	HpCDD	0.84*	III
Soil	OCDD	0.98*	V
Soil	PeCDF	1.00*	IV
Soil	HpCDF	0.94*	III
Fly-Ash	OCDD	0.97*	V
Fly-Ash	TCDF	0.89*	V
Fly-Ash	PeCDF	0.91*	III
Fly-Ash	HpCDF	0.98*	IV
Sludge	HpCDD	0.87*	IV

*Significant at the 5 percent level ($\alpha = 0.05$).
Note: This Table lists only those matrix/analyte combinations with significant G-statistics. All other combinations were not significant.

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Appendix A

Definition and Procedure for the Determination of the Method Detection Limit

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero and determined from analysis of a sample in a given matrix containing analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

   (a) The concentration value that corresponds to an instrument signal/noise ratio in the range of 2.5 to 5. If the criteria for qualitative identification of the analyte is based upon pattern recognition techniques, the least abundant signal necessary to achieve identification must be considered in making the estimate.
   (b) The concentration value that corresponds to three times the standard deviation of replicate instrumental measurements for the analyte in reagent water.
   (c) The concentration value that corresponds to the region of the standard curve where there is a significant change in sensitivity at low analyte concentrations, i.e., a break in the slope of the standard curve.
   (d) The concentration value that corresponds to known instrumental limitations.

   It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent water (blank), prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated MDL. (Recommend between 1 and 5 times the estimated MDL.) Proceed to Step 4.

   (b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated MDL, proceed to Step 4.

   If the measured concentration of analyte is less than the estimated MDL, add a known amount of analyte to bring the concentration of analyte to between one and five times the MDL. In the case where an interference is coanalyzed with the analyte.

   If the measured level of analyte is greater than five times the estimated MDL, there are two options.

   (1) Obtain another sample of lower level of analyte in same matrix if possible.
   (2) The sample may be used as is for determining the MDL if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the MDL and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If blank measurements are required to calculate the measured level of analyte, obtain separate blank measurements for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.
   (b) It may be economically and technically deirable to evaluate the estimated MDL before proceeding with 4a. This will: (1) prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an incorrect MDL can be calculated from data obtained at many times the real MDL even though the background concentration of analyte is less than five times the calculated MDL. To insure that the estimate of the MDL is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower MDL. Take two aliquots of the sample to be used to calculate the MDL and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

   (1) If these measurements indicate the sample is in the desirable range for determining the MDL, take five additional aliquots and proceed. Use all seven measurements to calculate the MDL.
   (2) If these measurements indicate the sample is not in the correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2 \Big/ n\right]$$

$$S = (S^2)^{1/2}$$

where: the x_i, i = 1 to n are the analytical results in the final method reporting units obtained from the n sample aliquots and $\sum_{i=1}^{n} X_i^2$ refers to the sum of the X values from i = 1 to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,\ 1-\alpha\ =\ 99)}(S)$$

where:

MDL = the method detection

$t_{(n-1,\ 1-\alpha\ =\ 99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence limits for the MDL derived in 6a are computed according to the following equations de ived from percentiles of the chi square over degrees of freedom distribution (X^2/df) and calculated as follows:

MDL_{LCL} = 0.69 MDL
MDL_{UCL} = 1.92 MDL

where MDL_{LCL} and MDL_{UCL} are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimated MDL and calculated MDL of subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimated MDL in Step 1, take the MDL as calculated in Step 6, spike in the matrix at the calculated MDL and proceed through the procedure starting with Step 4.
(b) If the current MDL determination is an iteration of the MDL procedure for which the spiking level does not permit qualitative identification, report the MDL as that concentration between the current spike level and the previous spike level which allows qualitative identification.
(c) If the current MDL determination is an iteration of the MDL procedure and the spiking level allows qualitative identification, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F ratio.

$$\text{if } \frac{S_A^2}{S_B^2} < 3.05$$

then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{1/2}$$

if $\frac{S_A^2}{S_B^2} > 3.05$, respike at the last calculated MDL and process the samples through the procedure starting with Step 4.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

$$MDL = 2.681\ (S_{pooled})$$

where 2.681 is equal to $t_{(12,\ 1-\alpha\ =\ .99)}$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

$$MDL_{LCL} = 0.72\ MDL$$
$$MDL_{UCL} = 1.65\ MDL$$

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with the MDL value. Report the mean analyte level with the MDL. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, report the mean recovery, and indicate if the MDL determination was iterated.

If the level of the analyte in the sample matrix exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

Reference

Glaser, J. A., Foerst, D. L., McKee, G. D., Quave, S. A., and Budde, W. L., "Trace Analysis for Wastewaters," *Environmental Science and Technology, 15,* 1426 (1981).

Table of Students' t Values at the 99 Percent Confidence Level

Number of Replicates	*Degrees of Freedom (n-1)*	$t_{(n-1,\ 1-\alpha\ =\ .99)}$
7	*6*	*3.143*
8	*7*	*2.998*
9	*8*	*2.896*
10	*9*	*2.821*
11	*10*	*2.764*
16	*15*	*2.602*
21	*20*	*2.528*
26	*25*	*2.485*
31	*30*	*2.457*
61	*60*	*2.390*
∞	∞	*2.326*

APPENDIX B

RCRA METHOD 8280 WITH REVISIONS BASED ON MULTI-LABORATORY TESTING:
METHOD OF ANALYSIS FOR CHLORINATED DIBENZO-P-DIOXINS
AND DIBENZOFURANS

1. Scope and Application

1.1 This method is appropriate for the determination of total tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins and dibenzofurans in chemical wastes including still bottoms, filter aids, sludges, spent carbon, fly ash, reactor residues, soil, and water.

1.2 The sensitivity of this method is dependent upon the level of interferents within a given matrix. Target quantification levels of individual analytes were 1 ppb in solid samples and 10 ppt in water.

1.3 This method is recommended for use only by analysts experienced with residue analysis and skilled in mass spectral analytical techniques.

1.4 Because of the extreme toxicity of these compounds, the analyst must take necessary precautions to prevent exposure to himself, or to others, of materials known or believed to contain PCDD's or PCDF's. Typical infectious waste incinerators are probably not satisfactory devices for disposal of materials highly contaminated with PCDD's or PCDF's. Generators of 1 Kg or more of dioxin wastes must register as a generator. A laboratory planning to use these compounds should prepare a disposal plan to be reviewed and approved by the Dioxin Task Force of the EPA (Contact Conrad Kleveno, WH-548A, U.S. EPA, 401 M Street S.W., Washington, D.C. 20450). Additional safety instructions are outlined in EPA Test Method 613.

2. Summary of the Method

2.1 This procedure is an extraction, cleanup, and high resolution capillary column gas chromatography-low resolution mass spectrometry method using internal standard techniques which allow for the measurement of PCDD's and PCDF's in the extract.

2.2 If interferents are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. The analysis flow chart is shown in Figure 1.

3. Interferents

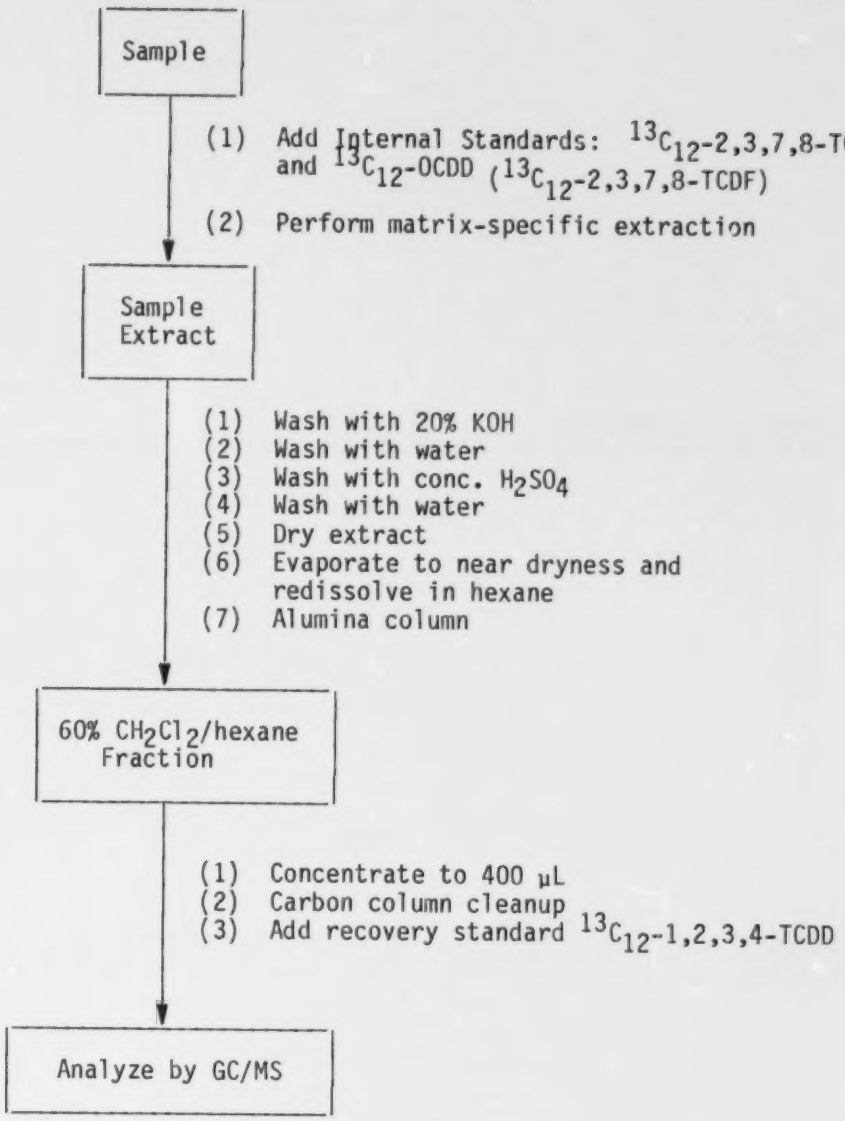
Sample
(1) Add Internal Standards: $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-OCDD ($^{13}C_{12}$-2,3,7,8-TCDF)
(2) Perform matrix-specific extraction
Sample Extract
(1) Wash with 20% KOH
(2) Wash with water
(3) Wash with conc. H_2SO_4
(4) Wash with water
(5) Dry extract
(6) Evaporate to near dryness and redissolve in hexane
(7) Alumina column
60% CH_2Cl_2/hexane Fraction
(1) Concentrate to 400 µL
(2) Carbon column cleanup
(3) Add recovery standard $^{13}C_{12}$-1,2,3,4-TCDD
Analyze by GC/MS

Figure 1. Method 8280 flow chart for the analysis of PCDD's and PCDF's.

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts or elevated baselines or both which may cause misinterpretation of chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running method blanks. Solvents distilled in all-glass systems are required.

3.2 Interferents co-extracted from the sample will vary considerably from source to source and will depend upon the industrial process being sampled. PCDD's and PCDF's are often associated with other interfering chlorinated compounds such as PCB's and polychlorinated diphenyl ethers which may be found at concentrations several orders of magnitude higher than that of the analytes of interest. Retention times of target analytes must be verified using reference standards. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup techniques to achieve the method detection levels stated in Table 9.

3.3 Resolution of the 2,3,7,8-TCDD isomer from other closely eluting TCDD's must be used to establish column performance criteria. High resolution capillary columns are used to resolve as many PCDD and PCDF isomers as possible; however, no single column is known to resolve all of the isomers in a complex mixture.

4. Apparatus and Materials

4.1 Sampling equipment for discrete or composite sampling.

4.1.1 Grab sample bottle--amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be acid washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps--threaded to screw onto the sample bottles. Caps must be lined with Teflon. Solvent washed foil used with the shiny side toward the sample may be substituted for Teflon if the sample is not corrosive. Apply tape around cap to completely seal cap to bottle.

4.1.3 Compositing equipment--automatic or manual compositing system. No tygon or rubber tubing may be used, and the system must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated after sampling.

4.2 Water bath--heated, with concentric ring cover, capable of temperature control ($\pm$2°C). The bath should be used in a hood.

4.3 Gas chromatograph/mass spectrometer data system.

4.3.1 Gas chromatograph: An analytical system with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.3.2 Fused silica capillary columns are required. As shown in Table 1, four columns were evaluated using a column performance check mixture containing 1,2,3,4-TCDD, 2,3,7,8-TCDD, 1,2,3,4,7-PeCDD, 1,2,3,4,7,8-HxCDD,

1,2,3,4,6,7,8-HpCDD, OCDD, and 2,3,7,8-TCDF.

The columns include the following: (a) 50 m CP-Sil-88 programmed 60°-190° at 20°/minute, then 190°-240° at 5°/minute; (b) 30 m DB-5 programmed 170° for 10 minutes, then 170°-320° at 8°/minute, hold at 320°C for 20 minutes; (c) 30 m SP-2250 programmed 70°-320° at 10°/minute; (d) 30 m DB-225 programmed 70° - 230° at 10°/minute. Column/conditions (a) provide good separation of 2,3,7,8-TCDD from the other TCDD's at the expense of longer retention times for higher homologs. Column/conditions (b) and (c) can also provide acceptable separation of 2,3,7,8-TCDD. Resolution of 2,3,7,8-TCDD from the other TCDD's is better on column (c), but column (b) is more rugged and may provide better separation from certain classes of interferents.

4.3.3 Mass spectrometer: Capable of scanning from 222 to 506 amu in not less than 5 seconds, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets the criteria in Table 2 when a mass calibration using perfluoro-tri-n-butylamine (FC-43) is performed. The system must also be capable of selected ion monitoring (SIM) for at least nine ions simultaneously, with a cycle time of 1 sec or less. Minimum integration time for SIM is 50 ms. Acceptable selected ion monitoring is verified by injecting 0.15 ng of native TCDD to give a minimum signal-to-noise ratio of 5 to 1 at m/z 320.

4.3.4 GC/MS interface: Any GC-to-MS interface that gives an acceptable calibration response for each analyte of interest at the concentration required and achieves the required tuning performance criteria (see Sections 6.1-6.3) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are required. Glass can be deactivated by silanizing with dichlorodimethylsilane. Inserting a fused silica column directly into the MS source is recommended.

4.3.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow for the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be able to integrate the abundance, in any EICP, between specified time or scan number limits.

4.3.6 HPLC pump with loop valve (1.0 mL) injector to be used in the carbon column cleanup procedure.

4.4 Pipettes-Disposable, Pasteur, 150 mm long x 5 mm ID (Fisher Scientific Company, No. 13-678-6A, or equivalent).

4.5 Amber glass bottle (500 mL, Teflon-lined screw cap).

4.6 Reacti-vial 1 mL, amber glass (silanized) (Pierce Chemical Company).

4.7 500 mL Erlenmeyer flask (American Scientific Products Cat. No. f4295-500f0) fitted with Teflon stoppers (ASP No. s9058-8, or equivalent).

4.8 Wrist Action Shaker (VWR No. 57040-049, or equivalent).

4.9 125 mL and 2 L Separatory Funnels (Fisher Scientific Company, No. 10-437-5b, or equivalent).

4.10 500 mL Kuderna-Danish fitted with a 10 mL concentrator tube and 3-ball Snyder column (Ace Glass No. 6707-02, 6707-12, 6575-02, or equivalent).

4.11 Teflon boiling chips (Berghof/American Inc., Main St., Raymond, New Hampshire 03077, No. 15021-450, or equivalent). Wash with hexane prior to use.

4.12 300 mm x 10.5 mm glass chromatographic column fitted with Teflon stopcock.

4.13 15 mL conical concentrator tubes (Kontes No. K-288250, or equivalent).

4.14 Adaptors for concentrator tubes (14/20 to 19/22) (Ace Glass No. 9092-20, or equivalent).

4.15 Nitrogen evaporator (N-Evap No. 1156, or equivalent). Teflon tubing connection to trap and gas regulator is required.

4.16 Microflex conical vials (Kontes K-749000, or equivalent).

4.17 Filter paper (Whatman No.54, or equivalent).

4.18 Carbon Column: A silanized glass HPLC column (10 mm x 7 cm), or equivalent, prepared by mixing 5 percent (by weight) active carbon AX-21, (Anderson Development Co., Adrian, Michigan), washed with methanol and dried in vacuo at 110°C, and 10 µm silica (Spherisorb S10W from Phase Separations, Inc., Norwalk, Connecticut). The mixture must be stirred and sieved through a 38 µm screen (U.S. Sieve Designation 400-mesh, American Scientific Products, No. S1212-400, or equivalent) to remove any clumps.1/

4.19 Dean-Stark trap, 5 or 10 mL with T joints, (Fisher Scientific Company, No. 09-146-5, or equivalent) condenser and 125-mL flask.

5. Reagents

5.1 Potassium hydroxide-(ACS), 20 percent (w/v) in distilled water.

5.2 Sulfuric acid-(ACS), concentrated.

5.3 Methylene chloride, hexane, benzene, petroleum ether, methanol, tetradecane, isooctane, toluene, cyclohexane. Distilled in glass.

1/ - The carbon column preparation and use is adapted from W. A. Korfmacher, L. G. Rushing, D. M. Nestorick, H. C. Thompson, Jr., R. K. Mitchum, and J. R. Kominsky, Journal of High Resolution Chromatography and Chromatography Communications, 8, 12-19 (1985).

5.4 Prepare stock standards in a glovebox from concentrates or neat materials. The stock solutions are stored in the dark at 4°C and are checked frequently for signs of degradation or evaporation especially just prior to the preparation of working standards.

5.5 Alumina, neutral, Super 1, Woelm, 80/200 mesh. Store at room temperature in a desiccator with $CaSO_4$ drying agent. Oven drying at 600°C overnight is acceptable, but alumina so processed should be checked for contamination by solvent rinsing and GC/ECD analysis.

5.6 Prepurified nitrogen gas.

5.7 Anhydrous sodium sulfate (reagent grade). Extracted overnight with hexane using a Soxhlet extraction apparatus and dried at 100°C.

6. Calibration

6.1 Before using any cleanup procedure, the analyst must process a series of calibration standards (Section 11) through the procedure to validate elution patterns and the absence of interferents from reagents. Both open column and carbon column performance must be checked. Routinely check the 8 percent CH_2Cl_2/hexane eluate of environmental extracts from the alumina column for presence of target analytes.

6.2 Prepare multi-level calibration standards[2/] keeping the recovery standard ($^{13}C_{12}$-1,2,3,4-TCDD) and the internal standard ($^{13}C_{12}$-2,3,7,8-TCDD) at fixed concentrations of 500 ng/mL. A second internal standard, $^{13}C_{12}$-OCDD, at a fixed concentration of 1000 ng/mL is recommended for use when quantification of the hepta- and octa-isomers is required. The use of separate internal standards for the PCDF's is also recommended. Recommended concentration levels for standard analytes (Section 11.1.3) are 200, 500, 1000, 2000, and 5000 ng/mL. Calculation of response factors is described in Section 11.2. Standards must be analyzed using the same solvent as used in the final extract; toluene is recommended. A wider calibration range is useful for higher level samples provided it can be described within the linear range of the method.

6.3 Establish operating parameters for the GC/MS system; the instrument should be tuned to meet the isotopic ratio criteria listed in Table 2 for FC-43. By injecting calibration standards, establish the response factors of standards vs. the appropriate internal standard. (PCDF response factors are established vs. $^{13}C_{12}$-2,3,7,8-TCDF if this standard is used). Response factors for the hepta- and octa-chlorinated CDD's and CDF's are to be calculated using the corresponding $^{13}C_{12}$-octachlorinated standards as described in Section 11.2.

2/ - $^{13}C_{12}$-labeled analytes are available from Cambridge Isotope Laboratory, Woburn, Massachusetts. Proper standardization requires the use of a specific labeled isomer for each congener to be determined. When labeled PCDD's and PCDF's of each homolog are available, their use will be required to be consistent with the technique of isotopic dilution mass spectral analysis.

6.4 An adequate instrumental detection limit should be verified by injecting 0.15 ng of $^{13}C_{12}$-2,3,7,8-TCDD which should give a minimum signal to noise ratio of 5 to 1 at m/z 334. GC column performance should be checked for resolution and peak shape daily using a mixed standard such as the GC column performance check mixture described in Section 4.3.2.

7. Quality Control

7.1 Before processing any samples, the analyst must demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interferent-free at the method detection limit of the matrix of interest. Each time a set of samples is extracted, or there is a change in reagents, a method blank must be processed as a safeguard against laboratory contamination.

7.2 Standard quality assurance practices must be used with this method. Field replicates must be collected to validate the precision of the sampling technique. Laboratory replicates must be analyzed to determine the precision of the analysis. Fortified samples must be analyzed to establish the accuracy of the analysis. Field blanks must be collected to verify that sample collection processes are free from cross-contamination.

8. Sample Collection, Preservation, and Handling

8.1 Grab and composite samples must be collected in glass containers. Conventional sampling practices must be followed. The bottle must not be pre-washed with sample before collection. Composite samples should be collected in glass containers. Sampling equipment must be free of tygon, rubber tubing and other potential sources of contamination.

8.2 All samples must be stored at 4°C, extracted within 7 days, and completely analyzed within 30 days of collection.

9. Extraction and Cleanup Procedures

9.1 Internal standard addition. Use a sample aliquot of 0.1-10 g (typical sample size requirements for each type of matrix is provided in Section 9.2) of the chemical waste or soil to be analyzed. Transfer the sample to a tared flask and determine the weight of the sample. Add an appropriate quantity of $^{13}C_{12}$-2,3,7,8-TCDD and any other material which is used as an internal standard, (Section 6.2). All samples should be spiked with at least one internal standard, for example, $^{13}C_{12}$-2,3,7,8-TCDD, to give an approximate concentration of 500 pg/µL in the final concentrated extract. As an example, a 10 g sample concentrated to a final volume of 100 µL requires the addition of 50 ng of $^{13}C_{12}$-2,3,7,8-TCDD at 100% recovery.

9.2 Extraction

9.2.1 Sludge. Extract aqueous sludge samples by refluxing a sample (e.g., 2 g) with 50 mL of toluene in a 125 mL flask fitted with a Dean-Stark water separator. Continue refluxing the sample until all the water has been removed. Cool the sample, filter the toluene extract through Whatman No. 54 filter paper or equivalent into a 100 mL round bottom flask. Rinse the filter with 10 mL

of toluene, combine the extract and rinseate. Concentrate the combined solution to near dryness using a rotary evaporator at 50°C. Use of an inert gas to concentrate the extract is also permitted. Proceed with step 9.2.4.

9.2.2 Still bottom. Extract still bottom samples by mixing a sample (e.g., 0.1 g) with 10 mL of toluene and filtering the solution through Whatman No. 54 filter paper (or equivalent) into a 50 mL round bottom flask. Rinse the filter with 10 mL of toluene. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C. Proceed with step 9.2.4.

9.2.3 Fly ash. Extract fly ash samples by placing a sample (e.g., 10 g) and an equivalent amount of anhydrous sodium sulfate in a Soxhlet extraction apparatus charged with toluene; extract for 16 hours using a three cycle/hour schedule. Cool and filter the toluene extract through Whatman No. 54 filter paper (or equivalent) into a 500 mL round bottom flask. Rinse the filter with 5 mL of toluene. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C. Proceed with step 9.2.4.

9.2.4 Transfer the residue to a 125 mL separatory funnel using 15 mL of hexane. Rinse the flask with two 5 mL aliquots of hexane, and add the rinses to the funnel. Shake 2 minutes with 50 mL of 5% NaCl solution, discard the aqueous layer, and proceed with step 9.3.

9.2.5 Soil. Extract soil samples by placing the sample (e.g., 10 g) and an equivalent amount of anhydrous sodium sulfate in a 500 mL Erlenmeyer flask fitted with a Teflon stopper. Add 20 mL of methanol and 80 mL of petroleum ether (in that order) to the flask. Shake on a wrist-action shaker for two hours. The solid portion of sample should mix freely. If a smaller soil sample is used, scale down the amount of methanol proportionally.

9.2.5.1 Filter the extract from Section 9.2.5 through a glass funnel fitted with filter paper (Whatman No. 54, or equivalent) and filled with anhydrous sodium sulfate into a 500 mL Kuderna-Danish (KD) concentrator fitted with a 10 mL concentrator tube. Add 50 mL of petroleum ether to the Erlenmeyer flask, restopper the flask, and swirl the sample gently; remove the stopper carefully and decant the solvent through the funnel as above. Wash the sodium sulfate on the funnel with two additional 5 mL portions of petroleum ether.

9.2.5.2 Add a Teflon boiling chip and a three-ball Snyder column to the KD flask. Concentrate in a 70°C steam bath to an apparent volume of 10 mL. Remove the apparatus from the steam bath, and allow it to cool for 5 minutes.

9.2.5.3 Add 50 mL of hexane and a new boiling chip to the KD flask. Concentrate in a steam bath to an apparent volume of 10 mL. Remove the apparatus from the steam bath, and allow it to cool for 5 minutes.

9.2.5.4 Remove and invert the Snyder column and rinse it down into the KD with two 1-mL portions of hexane. Decant the contents of the KD and concentrator tube into a 125 mL separatory funnel. Rinse the KD with two additional 5-mL portions of hexane; combine these rinsates in the separatory funnel. Proceed with step 9.3.

9.2.6 Aqueous samples. Mark the water meniscus on the side of the 1-L sample bottle for later determination of the exact sample volume. Pour the entire sample (approximately 1 L) into a 2-L separatory funnel. Note: A continuous liquid-liquid extractor may be used in place of a separatory funnel.

9.2.6.1 Add 60 mL methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel, and extract the sample by shaking the funnel for 2 minutes with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Collect the methylene chloride (3 x 60 mL) directly into a 500 mL Kuderna-Danish concentrator (mounted with a 10 mL concentrator tube) by passing the sample extracts through a filter funnel packed with a glass wool plug and 5 g of anhydrous sodium sulfate. After the third extraction, rinse the sodium sulfate with an additional 30 mL of methylene chloride to ensure quantitative transfer.

9.2.6.2 Attach a Snyder column, and concentrate the extract until the apparent volume of the liquid reaches 5 mL. Remove the K-D apparatus, and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, add 50 mL hexane, re-attach the Snyder column, and concentrate to approximately 5 mL. Rinse the flask and the lower joint with 2 x 5 mL hexane and combine rinses with extract to give a final volume of about 15 mL.

9.2.6.3 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed with Step 9.3

9.3 Partition the solvent against 40 mL of 20 percent (w/v) potassium hydroxide. Shake for 2 minutes. Remove and discard the aqueous layer (bottom). Repeat the base washing until no color is visible in the bottom layer (perform base washings a maximum of four times).

9.4 Partition the solvent against 40 mL of distilled water. Shake for 2 minutes. Remove and discard aqueous layer (bottom).

9.5 Partition the solvent against 40 mL of concentrated sulfuric acid. Shake for 2 minutes. Remove and discard the aqueous layer (bottom). Repeat the acid washings until no color is visible in the acid layer. (Perform acid washings a maximum of four times.)

9.6 Partition the extract against 40 mL of distilled water. Shake for 2 minutes. Remove and discard the aqueous layer (bottom). Dry the organic layer by pouring through a funnel containing anhydrous sodium sulfate, wash with two 5 mL portions of hexane, and concentrate the hexane solution to near dryness with a rotary evaporator (35°C water bath); make sure all traces of toluene are removed. (Use of an inert gas to concentrate the extract is also permitted).

9.7 Pack a gravity column (glass 300mm x 10.5mm) fitted with a Teflon stopcock in the following manner:

Insert a glass-wool plug into the bottom of the column. Add a 4 gram layer of sodium sulfate. Add a 4 gram layer of Woelm super 1 neutral alumina. Tap the top of the column gently. Woelm super 1 neutral alumina need not be activated or cleaned prior to use but should be stored in a sealed desiccator. Add a 4 gram layer of sodium sulfate to cover the alumina. Elute with 10 mL of hexane and close the stopcock just prior to the exposure of the sodium sulfate layer to air. Discard the eluant. Check the column for channeling. If channeling is present, discard the column. Do not tap a wetted column.

9.8 Dissolve the residue from 9.6 in 2 mL of hexane and apply the hexane solution to the top of the column. Elute enough hexane (3-4 mL) to complete the transfer of the sample cleanly to the surface of the alumina. Discard the eluant.

9.8.1 Elute with 10 mL of 8 percent (v/v) methylene chloride in hexane. As a quality assurance step, check that no PCDD's or PCDF's are eluted in this fraction.

9.8.2 Elute the PCDD's and PCDF's from the column with 15 mL of 60 percent (v/v) methylene chloride in hexane and collect this fraction in a conical shaped (15 mL) concentrator tube.

9.9 Carbon column cleanup.

Prepare a carbon column as described in section 4.18.

9.9.1 Using N_2, gently concentrate both fractions from the alumina column (Section 9.8) to about 1 mL. Wash the sides of the tube with a small volume (1-2 mL) of hexane and reconcentrate to about 1 mL. Save the 8 percent fraction for GC/MS injection to check for any bleedthrough of PCDD's and PCDF's (a quality assurance step). Evaporate the 60 percent CH_2Cl_2/hexane fraction to about 400 µL and transfer to a HPLC injector loop (1.0 mL) for carbon column cleanup. Rinse the centrifuge tube with 500 µL hexane, and add both fractions to injector loop.

9.9.2 Elute the column at 2 mL/minute, ambient temperature, with 30 mL of cyclohexane/methylene chloride 1:1 (v/v). Discard the eluant. Next elute the column with 10 mL of CH_2Cl_2/MeOH/Benzene 70:20:5 (v/v). Discard the eluant. Backflush the column with 40 mL toluene to elute and collect PCDD's and PCDF's (entire fraction). The column is cleaned by pumping an additional 30 mL methanol followed by 40 mL of toluene in the back flush position. After returning the column to the original position, 30 mL of cyclohexane/methylene chloride 1:1 (v/v) is pumped through the column to re-equilibrate it in preparation for the next sample. The column must be replaced following the analysis of high level extracts (>500 ppb).

9.9.3 Evaporate the toluene fraction to about 1 mL on a rotary evaporator using a water bath at 50°C. Transfer to a 2.0 mL Reacti-vial using a toluene rinse and concentrate to the desired volume using a stream of N_2. The final volume should be 100 µL for soil samples and 500 µL for sludge, still bottom, and fly ash samples; the correct volume will depend on the relative concentration of target analytes. Extracts which are determined to be outside the

calibration range for individual analytes must be diluted, or a smaller sample must be re-extracted. Gently swirl the solvent on the lower portion of the vessel to ensure dissolution of the PCDD's and PCDF's.

9.10 Approximately 1 hour before HRGC/LRMS analysis, transfer an aliquot of the extract to a micro-vial. Add to this sufficient recovery standard ($^{13}C_{12}$-1,2,3,4-TCDD) to give a concentration of 500 ng/mL. (Example: 36 µL aliquot of extract and 4 µL of recovery standard solution. Remember to multiply final result by 10/9 to correct for this dilution. Inject an appropriate aliquot (1 or 2 µL) of the sample into the GC/MS instrument by using a syringe.

10. GC/MS Analysis

10.1 When toluene is employed as the final solvent, use of a bonded phase column from Section 4.3.2 is recommended. Solvent exchange into isooctance or tridecane is required for other liquid phases on nonbonded columns.

10.2 Calculate response factors for standards relative to the internal standards, $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-OCDD (see Section 11). Add the recovery standard to the samples prior to injection. The concentration of the recovery standard in the sample extract must be the same as that in the calibration standards used to measure the response factors.

10.3 Analyze samples with selected ion monitoring by using all of the ions listed in Table 3. It is recommended that the GC/MS run be divided into five scan-monitoring sections, namely: (1) 243, 257, 304, 306, 320, 322, 332, 334, 376 (TCDD's, TCDF's, $^{13}C_{12}$ internal and recovery standards, HxCDE); (2) 277, 293, 338, 340, 342, 354, 356, 358, 410 (PeCDD's, PeCDF's, HpCDE); (3) 311, 327, 372, 374, 376, 388, 390, 392, 446 (HxCDD's, HxCDF's, OCDE); (4) 345, 361, 406, 408, 410, 422, 424, 426, 480 (HpCDD's, HpCDF's, NCDE), and (5) 379, 395, 442, 444, 458, 460, 470, 472, 514 (OCDD, OCDF, $^{13}C_{12}$-OCDD, DCDE). Cycle time "not to exceed" 1 second/descriptor. HxCDE, HpCDE, OCDE, NCDE, DCDE are abbreviations for hexa-, hepta-, octa-, nona-, and deca-chlorinated diphenyl ether, respectively.

10.4 Identification criteria for individual PCDD's and PCDF's.

10.4.1 The retention time of the chromatographic peak (relative to that of $^{13}C_{12}$-2,3,7,8-TCDD) in the sample must match that in the standard mixture of available isomers within 0.01 units.

10.4.2 All of the characteristic ions, i.e., quantitation ion, confirmation ions, and the $[M\text{-}COCl]^+$ ion listed in Table 3 for each class of PCDD and PCDF, must be present.

10.4.3 The maximum intensity of each of the specified characteristic ions must coincide within ±1 scan.

10.4.4 The relative intensity of the selected, isotopic ions within the molecular ion cluster of a homologous series of PCDD's of PCDF's must lie within the range specified in Table 4.

10.5 Quantitate the PCDD and PCDF peaks from the response relative to the appropriate internal standard, $^{13}C_{12}$-2,3,7,8-TCDD or $^{13}C_{12}$-OCDD. Recovery of each internal standard ($^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-OCDD) vs. the recovery standard $^{13}C_{12}$-1,2,3,4-TCDD must be greater than 40 percent. Samples with recoveries of less than 40 percent or greater than 120 percent must be reextracted and reanalyzed.

10.5.1 In those circumstances where these procedures do not yield a definitive conclusion, the use of high resolution mass spectrometry or HRGC/MS/MS is suggested.

11. Calculations

11.1 Determine the concentration of individual isomers of tetra-, penta-, and hexa-CDD/CDF according to the equation:

$$\text{Concentration, ng/g} = \frac{Q_{is} \times A_s}{G \times A_{is} \times RF}$$

Where:

Q_{is} = ng of internal standard $^{13}C_{12}$-2,3,7,8-TCDD, added to the sample before extraction.

G = g of sample extracted.

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion (m/z 334) of the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

RF = response factor of the quantitation ion of the compound of interest relative to m/z 334 of $^{13}C_{12}$-2,3,7,8-TCDD.

11.1.1 Determine the concentration of individual isomers of hepta-CDD/CDF and the concentration of OCDD and OCDF according to the equation:

$$\text{Concentration, ng/g} = \frac{Q_{is} \times A_s}{G \times A_{is} \times RF}$$

Where:

Q_{is} = ng of internal standard $^{13}C_{12}$-OCDD, added to the sample before extraction.

G = g of sample extracted.

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion (m/z 472) of the internal standard, $^{13}C_{12}$-OCDD.

RF = response factor of the quantitation ion of the compound of interest relative to m/z 472 of $^{13}C_{12}$-OCDD.

Note: Any dilution factor introduced in section 9.10 should be applied to this calculation.

11.1.2 Response factors are calculated using data obtained from the analysis of multi-level calibration standards according to the equation:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion of the appropriate internal standard (m/z 334 for $^{13}C_{12}$-2,3,7,8-TCDD; m/z 472 for $^{13}C_{12}$-OCDD).

C_{is} = concentration of the appropriate internal standard, $^{13}C_{12}$-2,3,7,8-TCDD or $^{13}C_{12}$-OCDD.

C_s = concentration of the compound of interest.

11.1.3 The concentrations of unknown isomers of TCDD shall be calculated using the RF determined for 2,3,7,8-TCDD.

The concentrations of unknown isomers of PeCDD shall be calculated using the RF determined for 1,2,3,7,8-PeCDD or any available 2,3,7,8,X-PeCDD isomer.

The concentrations of unknown isomers of HxCDD shall be calculated using the RF determined for 1,2,3,4,7,8-HxCDD or any available 2,3,7,8,X,Y-HXCDD isomer.

The concentrations of unknown isomers of HpCDD shall be calculated using the RF determined for 1,2,3,4,6,7,8-HpCDD or any available 2,3,7,8,X,Y,Z-HpCDD isomer.

The concentrations of unknown isomers of TCDF shall be calculated using the RF determined for 2,3,7,8-TCDF.

The concentrations of unknown isomers of PeCDF shall be calculated using the RF determined for 1,2,3,7,8-PeCDF or any available 2,3,7,8,X-PeCDF isomer.

The concentrations of unknown isomers of HxCDF shall be calculated using the RF determined for 1,2,3,4,7,8-HxCDF or any available 2,3,7,8,X,Y-HxCDF isomer.

The concentrations of unknown isomers of HpCDF shall be calculated using the RF determined for 1,2,3,4,6,7,8-HpCDF or any available 2,3,7,8,X,Y,Z-HpCDF isomer.

The concentration of the octa-CDD and octa-CDF shall be calculated using the RF determined for each.

Mean Response factors for selected PCDD's and PCDF's are given in Table 5.

11.1.4 Calculate for each internal standard $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-OCDD the recovery, R_{is}, in the sample extract, using the equation:

$$R_{is} = \frac{A_{is} \times Q_{rs}}{A_{rs} \times RF_r \times Q_{is}} \times 100\%$$

Where:

A_{rs} = Area of quantitation ion (m/z 334) of the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD.

Q_{rs} = ng of recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD, added to extract.

The response factor for determination of recovery is calculated using data obtained from the analysis of the multi-level calibration standards according to the equation:

$$RF_r = \frac{A_{is} \times C_{rs}}{A_{rs} \times C_{is}}$$

Where:

C_{rs} = Concentration of the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD.

11.1.5 Calculation of total concentration of all isomers within each homologous series of PCDD's and PCDF's.

Total concentration of PCDD's or PCDF's = Sum of the concentrations of the individual PCDD or PCDF isomers

11.2 Report results in nanograms per gram; when duplicate and spiked samples are reanalyzed, all data obtained should be reported.

11.3 Accuracy and Precision. Table 6 gives the precision data for revised Method 8280 for selected analytes in the matrices shown. Table 7 gives recovery data for the same analyses. Table 8 gives the linear range and variation of response factors over the range for selected analyte standards. Table 9 gives estimated detection limits as measured in specific sample matrices.

TABLE 1. REPRESENTATIVE GAS CHROMATOGRAPH RETENTION TIMES* OF ANALYTES

Analyte	50 m CP-Sil-88	30 m DB-5	30 m SP-2250	30 m DB-225
2,3,7,8-TCDF	25.2	21.6	26.7	42.5
2,3,7,8-TCDD	23.6	22.2	26.7	37.3
1,2,3,4-TCDD	24.1	22.1	26.5	37.6
1,2,3,4,7-PeCDD	30.0	24.3	28.1	NM
1,2,3,4,7,8-HxCDD	39.5	26.4	30.6	NM
1,2,3,4,6,7,8-HpCDD	57.0	28.6	33.7	NM
OCDD	---	31.2	---	---

* Retention time in minutes, using temperature programs shown below.

NM = not measured.

Temperature Programs:

CP-Sil-88	60°C-190°C at 20°/minute; 190°-240° at 5°/minute.
30 m DB-5	170°, 10 minutes; then at 8°/minute to 320°C, hold at 320°C 20 minutes (until OCDD elutes).
SP-2250	70°-320° at 10°/minute.
DB-225	70°-230° at 10°/minute.

Column Manufacturers

CP-Sil-88	Chrompack Incorporated, Bridgewater, New Jersey
DB-5, DB-225	J and W Scientific, Incorporated, Rancho Cordova, California
SP-2250	Supelco, Incorporated, Bellefonte, Pennsylvania

TABLE 2. CRITERIA FOR ISOTOPIC RATIO MEASUREMENTS FOR FC-43 CALIBRATION[a]

Selected Ions (m/z)	Intensity Ratio
232/231	3.8 - 7.0
265/264	3.8 - 7.0
315/314	4.5 - 8.4
415/414	6.0 - 11.2
465/464	6.8 - 12.6
503/502	6.8 - 12.6

[a] Scan from m/z 222 to m/z 506; nominal scan time 5 sec.

TABLE 3. IONS SPECIFIED[a] FOR SELECTED ION MONITORING FOR PCDD'S AND PCDF'S

	Quantitation Ion	Confirmation Ions	M-COCl
PCDD's			
$^{13}C_{12}$-Tetra	334	332	---
Tetra	322	320	257
Penta	356	354; 358	293
Hexa	390	388; 392	327
Hepta	424	422; 426	361
Octa	460	458	395
$^{13}C_{12}$-Octa	472	470	
PCDF's			
Tetra	306	304	243
Penta	340	338; 342	277
Hexa	374	372; 376	311
Hepta	408	406; 410	345
Octa	444	442	379

[a] Ions at m/z 376 (HxCDE), 410 (HpCDE), 446 (OCDE), 480 (NCDE) and 514 (DCDE) are also included in the scan monitoring sections (1) to (5), respectively. See Section 10.3.

TABLE 4. CRITERIA FOR ISOTOPIC RATIO MEASUREMENTS FOR PCDD's AND PCDF's

	Selected ions (m/z)	Relative intensity
PCDD's		
Tetra	320/322	0.65-0.89
Penta	358/356	0.55-0.75
Hexa	392/390	0.69-0.93
Hepta	426/424	0.83-1.12
Octa	458/460	0.75-1.01
PCDF's		
Tetra	304/306	0.65-0.89
Penta	342/340	0.55-0.75
Hexa	376/374	0.69-0.93
Hepta	410/408	0.83-1.12
Octa	442/444	0.75-1.01

TABLE 5. MEAN RESPONSE FACTORS OF CALIBRATION STANDARDS

Analyte	RF[a]	RSD% (n = 5)	Quantitation Ion (m/z)
2,3,7,8-TCDD	1.01	32	322
1,2,3,7,8-PeCDD	0.96	10.6	356
1,2,3,4,7,8-HxCDD	0.80	10.8	390
1,2,3,4,6,7,8-HpCDD[b]	1.08	6.6	424
1,2,3,4,6,7,8-OCDD[b]	1.30	7.2	460
2,3,7,8-TCDF	1.51	3.9	306
1,2,3,7,8-PeCDF	1.48	13.8	340
1,2,3,4,7,8-HxCDF	1.29	13.4	374
1,2,3,4,6,7,8-HpCDF[b]	1.57	8.6	408
1,2,3,4,6,7,8-OCDF[b]	1.19	3.8	444
$^{13}C_{12}$-2,3,7,8-TCDD	1.00	-	334
$^{13}C_{12}$-1,2,3,4-TCDD	0.74	10.9	334
$^{13}C_{12}$-OCDD	1.00	-	472

[a] The RF value is the mean of the five determinations made. Nominal weights injected were 0.4, 1.0, 2.0, 4.0 and 10.0 ng.

[b] RF values for these analytes were determined relative to $^{13}C_{12}$-OCDD. All other RF's were determined relative to $^{13}C_{12}$-2,3,7,8-TCDD.

Instrument Conditions/Tune- GC/MS system was tuned as specified in Section 6.3. RF data was acquired under MID control, as specified in Section 10.3.

GC Program- The GC column was programmed as specified in Section 4.3.2(b).

TABLE 6. PRECISION DATA FOR REVISED METHOD 8280

Compound	Matrix[1]	Analyte Level (ng/g) Native	Native + Spike	N	Percent RSD
2,3,7,8-TCDD	clay	ND[2]	5.0	4	4.4
	soil	378	378	4	2.8
	sludge	ND	125	4	4.8
	fly ash	ND	46	2	-
	still bottom	487	487	3	24
1,2,3,4-TCDD	clay	ND	5.0	3	1.7
	soil	ND	25.0	4	1.1
	sludge	ND	125	4	9.0
	fly ash	38.5	84.5	4	7.9
	still bottom	ND	2500	2	-
1,3,6,8-TCDD	clay	ND	2.5	4	7.0
	soil	ND	25.0	4	5.1
	sludge	ND	125	4	3.1
	fly ash	19.1	65.1	2	-
	still bottom	227	2727	2	-
1,3,7,9-TCDD	clay	ND	2.5	4	19
	soil	ND	25.0	4	2.3
	sludge	ND	125.0	4	6.5
	fly ash	58.4	104.4	2	-
	still bottom	ND	2500	2	-
1,3,7,8-TCDD	clay	ND	5.0	4	7.3
	soil	ND	25.0	4	1.3
	sludge	ND	125	4	5.8
	fly ash	16.0	62.0	4	3.5
	still bottom	422	2920	2	-
1,2,7,8-TCDD	clay	ND	5.0	4	7.7
	soil	ND	25.0	4	9.0
	sludge	ND	125	4	7.7
	fly ash	2.6	48.6	3	23
	still bottom	ND	2500	2	-
1,2,8,9-TCDD	clay	ND	5.0	4	10
	soil	ND	25.0	4	0.6
	sludge	ND	125	4	1.9
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-

(continued)

TABLE 6. (Continued)

Compound	Matrix	Analyte Level (ng/g) Native	Native + Spike	N	Percent RSD
1,2,3,4,7-PeCDD	clay	ND	5.0	4	10
	soil	ND	25.0	4	2.8
	sludge	ND	125	4	4.6
	fly ash	25.8	71.8	4	6.9
	still bottom	ND	2500	2	-
1,2,3,7,8-PeCDD	clay	ND	5.0	4	25
	soil	ND	25.0	4	20
	sludge	ND	125	4	4.7
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-
1,2,3,4,7,8-HxCDD	clay	ND	5.0	4	38
	soil	ND	25.0	4	8.8
	sludge	ND	125	4	3.4
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-
1,2,3,4,6,7,8-HpCDD	clay	ND	5.0	4	4
	soil	ND	25.0	4	30.6
	sludge[3]	8966	9091	4	-
	fly ash	ND	-	-	-
	still bottom	ND	-	-	-
1,2,7,8-TCDF	clay	ND	5.0	4	3.9
	soil	ND	25.0	4	1.0
	sludge	ND	125	4	7.2
	fly ash	7.4	53.4	4	7.6
	still bottom	ND	2500	2	-
1,2,3,7,8-PeCDF	clay	ND	5.0	4	6.1
	soil	ND	25.0	4	5.0
	sludge	ND	125	4	4.8
	fly ash	ND	46	2	-
	still bottom[3]	25600	28100	2	-
1,2,3,4,7,8-HxCDF	clay	ND	5.0	4	26
	soil	ND	25.0	4	6.8
	sludge	13.6	139	4	5.6
	fly ash	24.2	70.2	4	13.5
	still bottom	ND	2500	2	-

(continued)

TABLE 6. (Continued)

Compound	Matrix	Analyte Level (ng/g) Native	Native + Spike	N	Percent RSD
OCDF	clay	ND	-	-	-
	soil	ND	-	-	-
	sludge	192	317	4	3.3
	fly ash	ND	-	-	-
	still bottom	ND	-	-	-

[1] matrix types:

clay: pottery clay, Westwood Ceramic Supply Co., City of Industry, California.

soil: Times Beach, Missouri, soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator; resource recovery ash No. 1.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production, obtained from Arthur D. Little, Inc., 1983.

sludge: sludge from cooling tower which received both creosote and pentachlorophenolic wastewaters.

Cleanup of clay, soil, and fly ash samples was through alumina column only. (Carbon column not used.)

[2] ND - not detected at concentration injected (final volume 0.1 ml or greater).

[3] Estimated concentration out of calibration range of standards.

[4] Not determined.

TABLE 7. RECOVERY DATA FOR REVISED METHOD 8280

Compound	Matrix[1]	Native[2] (ng/g)	Spiked[3] Level (ng/g)	Mean Percent Recovery
2,3,7,8-TCDD	clay	ND	5.0	61.7
	soil	378	-	-
	sludge	ND	125	90.0
	fly ash	ND	46	90.0
	still bottom	487	-	-
1,2,3,4-TCDD	clay	ND	5.0	67.0
	soil	ND	25.0	60.3
	sludge	ND	125	73.1
	fly ash	38.5	46	105.6
	still bottom	ND	2500	93.8
1,3,6,8-TCDD	clay	ND	2.5	39.4
	soil	ND	25.0	64.0
	sludge	ND	125	64.5
	fly ash	19.1	46	127.5
	still bottom	227	2500	80.2
1,3,7,9-TCDD	clay	ND	2.5	68.5
	soil	ND	25.0	61.3
	sludge	ND	125	78.4
	fly ash	58.4	46	85.0
	still bottom	ND	2500	91.7
1,3,7,8-TCDD	clay	ND	5.0	68.0
	soil	ND	25.0	79.3
	sludge	ND	125	78.9
	fly ash	16.0	46	80.2
	still bottom	422	2500	90.5
1,2,7,8-TCDD	clay	ND	5.0	68.0
	soil	ND	25.0	75.3
	sludge	ND	125	80.4
	fly ash	2.6	46	90.4
	still bottom	ND	2500	88.4
1,2,8,9-TCDD	clay	ND	5.0	59.7
	soil	ND	25.0	60.3
	sludge	ND	125	72.8
	fly ash	ND	46	114.3
	still bottom	ND	2500	81.2

(continued)

TABLE 7. (Continued)

Compound	Matrix[1]	Native[2] (ng/g)	Spiked[3] Level (ng/g)	Mean Percent Recovery
1,2,3,4,7-PeCDD	clay	ND	5.0	58.4
	soil	ND	25.0	62.2
	sludge	ND	125	79.2
	fly ash	25.8	46	102.4
	still bottom	ND	2500	81.8
1,2,3,7,8-PeCDD	clay	ND	5.0	61.7
	soil	ND	25.0	68.4
	sludge	ND	125	81.5
	fly ash	ND	46	104.9
	still bottom	ND	2500	84.0
1,2,3,4,7,8-HxCDD	clay	ND	5.0	46.8
	soil	ND	25.0	65.0
	sludge	ND	125	81.9
	fly ash	ND	46	125.4
	still bottom	ND	2500	89.1
1,2,3,4,6,7,8-HpCDD	clay	ND	5.0	ND
	soil	ND	25.0	ND
	sludge[4]	8966	125	-
	fly ash	ND	-	-
	still bottom	ND	-	-
2,3,7,8-TCDD (C-13)	clay	ND	5.0	64.9
	soil	ND	25.0	78.8
	sludge	ND	125	78.6
	fly ash	ND	46	88.6
	still bottom	ND	2500	69.7
1,2,7,8-TCDF	clay	ND	5.0	65.4
	soil	ND	25.0	71.1
	sludge	ND	125	80.4
	fly ash	7.4	46	90.4
	still bottom	ND	2500	104.5
1,2,3,7,8-PeCDF	clay	ND	5.0	57.4
	soil	ND	25.0	64.4
	sludge	ND	125	84.8
	fly ash	ND	46	105.8
	still bottom	25,600	2500	-

(continued)

TABLE 7. (Continued)

Compound	Matrix[1]	Native[2] (ng/g)	Spiked[3] Level (ng/g)	Mean Percent Recovery
1,2,3,4,7,8-HxCDF	clay	ND	5.0	54.2
	soil	ND	25.0	68.5
	sludge	13.6	125	82.2
	fly ash	24.2	46	91.0
	still bottom	ND	2500	92.9
OCDF	clay	ND	-	-
	soil	ND	-	-
	sludge	192	125	86.8
	fly ash	ND	-	-
	still bottom	ND	-	-

[1] matrix types:

clay: pottery clay, Westwood Ceramic Supply Co., City of Industry, California.

soil: Times Beach, Missouri soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator; resource recovery ash No. 1.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production, from Arthur D. Little, Inc. (1983).

sludge: sludge from cooling tower which received both creosote and pentachlorophenol wastewaters.

The clay, soil, and fly ash samples were subjected to alumina column cleanup, no carbon column was used.

[2] Final volume of concentrate 0.1 ml or greater, ND means below quantification limit, 2 or more samples analyzed.

[3] Amount of analyte added to sample, two or more samples analyzed.

[4] Estimated concentration out of calibration range of standards.

TABLE 8. LINEAR RANGE AND VARIATION OF RESPONSE FACTORS

Analyte	Linear Range Tested (pg)	n**	Mean RF	%RSD
1,2,7,8-TCDF*	50-6000	8	1.634	12.0
2,3,7,8-TCDD*	50-7000	7	0.721	11.9
2,3,7,8-TCDF	300-4000	5	2.208	7.9

* Response factors for these analytes were calculated using 2,3,7,8-TCDF as the internal standard. The response factors for 2,3,7,8-TCDF were calculated vs. $^{13}C_{12}$-1,2,3,4-TCDD.

** Each value of n represents a different concentration level.

TABLE 9. DETECTION LIMITS (ppb) FOR RCRA METHOD 8280[1,2]

Analyte Class	Clay	Soil	Fly Ash	Still Bottom[3]	Sludge
TCDD	1.0	5.0	1.0	500	25
TCDF	0.5	2.5	0.5	250	12
PeCDD	1.5	7.5	1.5	750	38
PeCDF	1.0	5.0	1.0	500	25
HxCDD	2.0	10	2.0	1000	50
HxCDF	1.5	7.5	1.5	750	38

1 The analytes of the class indicated were not quantified below this value. The instrument detection limit (S = 3 x Noise) for 2,3,7,8-TCDD in standards is 0.5 ppb when extrapolated for a 10 g sample concentrated to 100 µL.

2 Matrix types:

Clay: Pottery clay, Westwood Ceramic Supply Co., City of Industry, California.

Soil: Times Beach, Missouri, soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0. The 90 percent window was 143 to 469 ng/g.

Fly Ash: Ash from a municipal incinerator; resource recovery ash No. 1.

Still Bottom: Distillation bottoms (tar) from 2,4-dichlorophenol production, from Arthur D. Little, Inc. (1983).

Sludge: sludge from cooling tower which received both creosote and pentachlorophenolic wastewaters.

Cleanup of clay, soil and fly ash samples was through alumina column only, the carbon column not used.

3 The still bottom samples were not tested below this level due to high analyte levels found.